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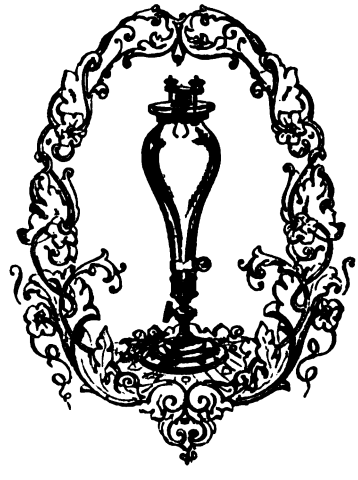

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HAND-BOOK

OF

CHEMISTRY.

BY

LEOPOLD GMELIN.

VOL. VIII.

ORGANIC CHEMISTRY,

VOL. II.

ORGANIC COMPOUNDS CONTAINING TWO AND FOUR ATOMS OF CARBON.

TRANSLATED BY

HENRY WATTS, B.A., F.C.S.

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CYANOGEN-COMPOUNDS.

(*Continued.*)

Dicyanide of Copper or Cuprous Cyanide. Cu^2Cy.—1. When hydrated dioxide of copper precipitated by potash from the solution of the dichloride in hydrochloric acid, and washed, is immersed in aqueous hydrocyanic acid, it is converted, with evolution of heat, into white dicyanide of copper. (Berzelius, Rammelsberg.) — 2. Hydrocyanic acid or cyanide of potassium added to a solution of dichloride of copper in hydrochloric acid forms a white, curdy precipitate. (Proust.)—3. The same precipitate is formed on adding hydrocyanic acid to solution of protochloride of copper mixed with sulphurous acid. (Berzelius.)—4. Protocyanide of copper heated beneath a watery liquid is converted into dicyanide. (Vauquelin, *Ann. Chim. Phys.* 9, 120.)

The white powder obtained by either of these methods fuses when heated, giving off a considerable quantity of water, and yielding a light brown-red, tumefied mass. (Gm.)—The compound, treated with nitric acid, gives off binoxide of nitrogen. It forms a colourless solution in aqueous ammonia, a yellow solution in strong hydrochloric acid, and is precipitated from the latter by potash. (Vauquelin.) Water likewise reprecipitates dicyanide of copper from its solution in hydrochloric acid. (Gm.)—This compound does not dissolve in warm dilute sulphuric acid. It dissolves in carbonate and succinate of ammonia, and likewise with the aid of heat, in sulphate, hydrochlorate, or nitrate of ammonia. (Wittstein.)

Dicyanide of copper unites with the cyanides of the alkali-metals, forming colourless salts, from which acids precipitate the dicyanide of copper in thick white flakes, with evolution of hydrocyanic acid.

Two-thirds Cyanide of Copper, or Cuproso-cupric Cyanide. α. $Cu^2Cy,CuCy$.—Known only in the hydrated state. Vauquelin (*Ann. Chim. Phys.* 9, 120), and Pagenstecher (*N. Tr.* 3, 1, 451), who first examined this compound, appear to have taken it for protocyanide of copper; Wöhler (*Pogg.* 1, 236) found that its formation is attended with evolution of cyanogen, and Rammelsberg (*Pogg.* 42, 121) confirmed the supposition (*Handb.* Aufl. 3, 1, 1264) that it is a mixture of dicyanide and protocyanide of copper.—1. Hydrated protoxide of copper immersed in aqueous hydrocyanic acid is converted into small, yellowish grey, crystalline granules. (Vauquelin.) — 2. Hydrocyanic acid added to sulphate of copper slowly throws down transparent, light green crystals. (Pagenstecher.) — 3. The brownish yellow hydrated protocyanide of copper precipitated by cyanide of potassium from a cold solution of a cupric salt, is gradually converted, with evolution of cyanogen, into the siskin-green cuproso-cupric cyanide. (Wöhler, Gm.) — 4. Cuproso-potassic cyanide, KCy,Cu^2Cy, forms the same precipitate with cupric

salts. (Rammelsberg).—The compound must be washed and dried at ordinary temperatures.

Siskin-green crystalline granules or transparent prisms, having a strong lustre.

This compound, when heated to 100°, gives off cyanogen and water, and without losing its crystalline form, is converted into white dicyanide of copper. (Rammelsberg.) When heated to 100° under water, it gives off cyanogen and becomes cream-coloured, according to Wöhler, white according to Gm.—Nitric acid dissolves the compound, with evolution of hydrocyanic acid, and forms a solution of nitrate of copper. (Rammelsberg.)—Hydrochloric acid also liberates hydrocyanic acid (Pagenstecher, Rammelsberg, Gm.), and, on the application of heat, dissolves the decolorized residue, forming a mixture of dichloride and protochloride of copper. (Gm.) Strong hydrochloric acid dissolves cuproso-cupric cyanide, even in the cold, forming a brown solution, which yields a white precipitate on the addition of water. (Gm.)—Aqueous solution of potash converts cuproso-cupric cyanide into cuproso-potassic cyanide, with separation of hydrated cupric oxide. (Gm.)

$$CuCy,Cu^2Cy + KO = KCy,Cu^2Cy + CuO.$$

On agitating the compound with potash, a blue filtrate is obtained, which when boiled, loses its colour and deposits black oxide of copper. (Rammelsberg.)—Aqueous ammonia dissolves the compound, forming a blue solution and leaving a blue residue. (Rammelsberg.)—Aqueous caustic ammonia (as stated by Scheele) and carbonate of ammonia dissolve the compound completely, even at ordinary temperatures; other ammonia-salts only with the aid of heat. (Wittstein.)—In an aqueous solution of cyanide of potassium, the compound assumes at first a yellow colour, because the cyanide of potassium dissolves the dicyanide most quickly and leaves the protocyanide; but afterwards the protocyanide is likewise converted into dicyanide and dissolved, with evolution of cyanogen. (Gm.)—The compound dissolves with green colour in aqueous solution of sulphate of copper. (Scheele.)—The author observed neither solution nor green colouring.

				Or:			
3 Cu	96	49·74		$3\ Cu^2Cy$	270	69·95	70·46
2 Cy	52	26·94		Cy	26	6·73	6·17
5 HO	45	23·32		10 HO	90	23·32	23·37
$Cu^2Cy,CuCy + 5Aq$	193	100·00			386	100·00	100·00

¶ Dufau (*Compt. rend.* 36, 1099) prepares this compound by passing into a tolerably dilute solution of a cupric salt, a solution equally dilute of cyanide of potassium or hydrocyanic acid, in such proportion as to leave a considerable quantity of the copper-salt undecomposed;—or by passing a stream of hydrocyanic acid vapour into water in which cupric oxide is suspended. The precipitate formed is yellow at first, but rapidly becomes green, and gives off a considerable quantity of cyanogen. The green precipitate, which has a crystalline aspect, contains 1 At. water, so that its formula is $Cu^2Cy,CuCy + Aq$. At 100° it gives off water without decomposing, but at higher temperatures it gives off cyanogen, and is converted into cuprous cyanide. Acids separate white cuprous cyanide from it, producing at the same time a cupric salt, and eliminating hydrocyanic acid. Caustic potash transforms it into cuprocyanide of potassium and cupric oxide. Ammonia dissolves it very

easily, forming a blue liquid which by spontaneous evaporation deposits beautiful green needles of biammoniacal cuproso-cupric cyanide. (*vid. inf.*)—It dissolves very readily in aqueous cyanide of potassium, forming a colourless or slightly bluish liquid, which soon changes to a crystalline mass having a nacreous aspect, and consisting of cuprocyanide of potassium; its formation is attended with evolution of cyanogen.

b. $2Cu^2Cy,CuCy + Aq$.—When a cupric salt is precipitated by a moderately concentrated solution of cyanide of potassium added in sufficient quantity to throw down nearly all the copper, an amorphous powder is obtained, of an olive-yellow colour, and a large quantity of cyanogen is given off: the precipitate has the composition above stated.—Both this compound and the preceding (*a*) are very instable, sometimes decomposing spontaneously, sometimes on the slightest rise of temperature, and—especially in presence of a large excess of hydrocyanic acid—giving off hydrocyanic acid, and leaving cuprous cyanide. (Dufau.) ¶

Protocyanide of Copper, or Cupric Cyanide. CuCy.—Known only in the hydrated state.—1. Carbonate of copper treated with aqueous hydrocyanic acid gives off carbonic acid, and forms brown-yellow protocyanide of copper. (Scheele.) — 2. Hydrocyanic acid added to acetate of copper immediately throws down the same compound. (Pagenstecher, *N. Tr.* 3, 1, 451.) — 3. Aqueous cyanide of potassium added, not in excess, to cold solutions of cupric salts, throws down brown-yellow protocyanide of copper. (Scheele.) This brown-yellow precipitate of hydrated protocyanide of copper decomposes spontaneously at ordinary temperatures into cyanogen gas and hydrated cuproso-cupric cyanide; and this mixture, when heated, gives off a large quantity of cyanogen, and is converted into white dicyanide of copper.—In consequence of this great tendency to decomposition, the properties of cupric cyanide are but little known.

Cuprocyanide of Ammonium. NH^4Cy,Cu^2Cy.—Exists, according to Monthiers (*N. J. Pharm.* 11, 257), who, however, says nothing more about it.—¶ In the preparation of biammoniacal cuproso-cupric cyanide (*vid. inf.*) by the action of hydrocyanic acid on cupric oxide suspended in ammonia, if the passage of the gas be continued after the needles of the green cyanide have been formed, these crystals first redissolve, then the liquid gradually becomes paler, and soon loses its colour completely. When concentrated and left to cool slowly, it deposits beautiful, colourless, prismatic needles of cuprocyanide of ammonium.—This compound, like the corresponding potassium-salt, is but slightly soluble in water, and like that salt also, decomposes when continuously boiled in that liquid. Heated to 100°, it gives off cyanide of ammonium; at a slightly higher temperature, it is rapidly converted into pure cuprous cyanide. (Dufau.) ¶

Ammoniacal Cuproso-cupric Cyanide. *a.* $NH^4Cy,2Cu^2Cy,HO$ — *Cuprocyanure de cuivre ammoniacal.*—Cupric sulphate forms with cuprocyanide of ammonium, a yellow precipitate, which, when washed and dried in vacuo, gives off cyanogen and turns green:

$$2(NH^4Cy,Cu^2Cy) + CuSO^3 + HO = NH^4Cu^5Cy^3,HO + NH^4O,SO^3 + Cy.$$

This precipitate is decomposed by acids and gives off ammonia when acted upon by fixed alkalis. (Monthiers.)

hydrocyanic acid. (Gm.) The same effect is produced by the salts of ferric and stannic oxide, excepting that the hydrates of these oxides are at the same time precipitated. (Ittner.) Mercuric salts throw down hydrocyanate of cupric oxide [dicyanide of copper] with formation of cyanide of mercury and a potash salt. Alkalis have no action on this compound. (Ittner.) The crystals dissolve sparingly in water, with partial separation of dicyanide of copper, whereby they become opaque, and afterwards crumble to a white powder. The solution when evaporated first yields crystals of the salt A, then of B; the former is therefore rendered soluble in water only through the medium of the latter. (Rammelsberg).

Crystallized.			Rammelsberg.	Monthiers.
4 C	24·0	15·46		15·6
2 N	28·0	18·04		18·2
2 Cu	64·0	41·24	40·55	41·0
K	39·2	25·26	26·03	25·2
KCy,Cu^2Cy	155·2	100·00		100·0

Cuprocyanide of Potassium B. $3KCy,Cu^2Cy$.—Discovered by Gm. (*Handb.* Aufl. 3, 1, 1268); more minutely examined by Rammelsberg (*Pogg.* 42, 124).—Preparation, the same as that of the salt A. In some cases, the salt A crystallizes first from the liquid, and afterwards the salt B; or if the quantity of cyanide of potassium present be considerable, the salt B crystallizes out alone. (Gm., Rammelsberg.) According to Prince Bagration (*J. pr. Chem.* 31, 367), copper dissolves in aqueous cyanide or ferrocyanide of potassium, and in this reaction, the same salt is produced together with free potash (*comp.* Elsner, VII, 417).

Colourless, transparent, rhombic prisms, truncated on the lateral edges, and having 6-sided summits. (Gm.) Permanent in the air (Rammelsberg); acquires a bluish white tint after long keeping. (Gm.)—The crystals decrepitate when heated, and at a temperature much below redness, they fuse without loss of water, and form a liquid which is likewise blue by transmitted, and brown-red by reflected light, and does not undergo any further decomposition at a moderate red heat; on cooling, it solidifies into a mass coloured reddish white by admixed particles of copper.—Small quantities of the stronger acids precipitate dicyanide of copper from the solution, and liberate hydrocyanic acid. (Gm.) A similar effect is produced by ferric salts, a precipitate of hydrated ferric oxide being, however, formed at the same time. (Rammelsberg.) Mercurous nitrate forms a green precipitate. (Gm.)—The salt dissolves readily in water, and its warm concentrated solution takes up a considerable quantity of the salt A, so that as it cools, crystals of A separate out. (Rammelsberg.) The solution of the salt B forms a pale yellow precipitate with cupric salts. (Gm., F. & E. Rodgers.) This precipitate should be: Cu^4Cy^5.

Crystallized.			Rammelsberg.
3 K	117·6	41·17	41·09
2 Cu	64·0	22·41	22·35
4 Cy	104·0	36·42	
$3KCy,Cu^2Cy$	285·6	100·00	

¶ *Cuprocyanide of Potassium C.* $2KCy,3Cu^2Cy$.—Formed by the action of potash on fused dicyanide of copper. (Rammelsberg, *Pogg.* 64, 65.) ¶

Cuprocyanide of Sodium.—Formed by precipitating the solution of red cuprocyanide of barium with an equivalent quantity of sulphate of soda, and evaporating the filtrate, which contains purpurate of soda as well as cyanide of copper and sodium; the former of these salts effloresces at the edge, while the cuprocyanide of sodium remains in the basin i)the form of small needles, which are permanent in the air. (Meillet, *N. J. Pharm.* 3, 413.)

Cuprocyanide of Barium.—When aqueous hydrocyanic acid is poured upon a mixture of carbonate of copper and hydrate of baryta, the whole dissolves with brisk effervescence. The carmine-coloured precipitate formed by purpurate of ammonia is evaporated, whereby it gradually loses its colour. Water poured upon the residue dissolves out the colourless cuprocyanide of barium, leaving a residue of carbonate of baryta. (Meillet.)

Cuprocyanide of Uranium?—Cuprocyanide of potassium B added to hydrochlorate of uranic oxide throws down a pale yellow powder. (Gm.)

Cuprocyanide of Manganese.—*a.* Cuprocyanide of potassium A forms with manganous salts a yellowish white precipitate, which dissolves in acids with evolution of hydrocyanic acid. (Ittner.)—*b.* Cuprocyanide of potassium B forms a white precipitate with manganous salts. (Gm.)

Sesquicyanide of Manganese and Copper.—Sesquicyanide of manganese and potassium forms a grey precipitate with cupric salts. (Rammelsberg.)

Cuprocyanide of Bismuth.—Cuprocyanide of potassium A forms with bismuth-salts a yellowish white precipitate, which dissolves in acids with evolution of hydrocyanic acid. (Ittner.)

Cuprocyanide of Zinc.—*a.* Cuprocyanide of potassium forms with zinc-salts a white precipitate, which dissolves in acids with separation of hydrocyanic acid. (Ittner.)—*b.* The copper-salt B yields curdy white flakes. (Gm.)

Cuprocyanide of Cadmium.—Cyanide of cadmium and potassium added to solution of sulphate of copper throws down a brownish white precipitate, with evolution of cyanogen gas. (Rammelsberg.)

Cuprocyanide of Tin.—Cuprocyanide of potassium B forms a white, curdy precipitate with protochloride of tin. (Gm.)

Cuprocyanide of Lead.—*a.* Cuprocyanide of potassium forms, with lead-salts, a whitish-green precipitate (white, according to Rammelsberg), which dissolves in acids with evolution of hydrocyanic acid. (Ittner.)—*b.* The copper-salt B precipitates lead-salts in fine, white, curdy flakes. (Gm.)

Cuprocyanide of Iron.—*a.* Cuprocyanide of potassium A forms, with ferric salts, a greenish yellow precipitate, from which acids dissolve out dicyanide of copper, leaving a residue of protocyanide of iron. (Ittner.) The precipitate is white, but turns yellow when exposed to the air, the surface becoming yellowish green. (Rammelsberg.)—*b.* Cuprocyanide of potassium B forms a yellow precipitate, which turns greenish on exposure to the air (Rammelsberg); according to F. & E. Rodgers, the precipitate

is white. With green vitriol free from ferric oxide, the author obtained no precipitate.

Cuprous Ferrocyanide. Cu^4FeCy^3?—Ferrocyanide of potassium added to a solution of dichloride of copper in hydrochloric acid throws down white flakes which, when exposed to the air, or to the action of chlorine-water, become purple-red from formation of the following compound. (Proust, *A. Gehl.* 6, 578.) The precipitate immersed in ammonia turns grey and dissolves, but it is not soluble in ammoniacal salts. (Wittstein.)

Cupric Ferrocyanide. $C^6N^3FeCu^2 = Cu^2FeCy^3$.—Ferrocyanide of potassium added to excess of a cupric salt forms a dark purple-red precipitate. The liquids, if concentrated, solidify in a magma when stirred; if more dilute, they yield thick flakes; and if very dilute, the mixture assumes a beautiful red colour.—This precipitate, even when a large excess of copper-salt is used, carries down with it a large quantity of ferrocyanide of potassium, so that it may contain as much as 5 per cent. of potassium. (Mosander.) The potassium-salt cannot be removed by continued washing. If, therefore, the precipitate be suspended in water, and decomposed by sulphuretted hydrogen—which takes a long time—a strongly acid liquid is obtained which, like hydroferrocyanic acid, deposits prussian blue on exposure to the air, and forms a blue precipitate with ferric salts, but is not precipitated by ether, excepting on addition of hydrochloric acid. It contains $H^7KFe^4Cy^{12}$. (Williamson, *Ann. Pharm.* 57, 245).—¶ According to Rammelsberg (*Pogg.* 74, 65), acetate or sulphate of copper mixed with hydroferrocyanic acid, yields pure ferrocyanide of copper, which after drying over sulphuric acid, contains $Cu^2FeCy^3 + 7\ Aq$; according to Monthiers, however, it contains 9 Aq. —When a cupric salt is added drop by drop to excess of ferrocyanide of potassium, the precipitate formed consists, according to Mosander, of the anhydrous compound $KCu,FeCy^3$; but according to Rammelsberg, it contains 2 At. water, and its composition is expressed by the improbable formula $Cu^2FeCy^3 + KCy,FeCy + 2Aq$. When, on the other hand, ferrocyanide of potassium is added by drops to excess of the cupric salt, a precipitate is formed consisting of $Cu^2FeCy^3,K^2FeCy^3,2Aq + 9(Cu^2FeCy^3,7Aq)$. (*Jahresber,* 1847-8, 478.) ¶

The salt gives up only a part of its water when gently heated, and at a stronger heat, evolves hydrocyanate of ammonia as well as water (Vauquelin), also carbonate of ammonia and nitrogen gas. (Berzelius). The residue, if more strongly heated in a retort, exhibits a faint glow, and appears afterwards to be composed of 1 At. bicarbide of iron and 2 At. monocarbide of copper. (Berzelius.)—Aqueous potash decomposes the salt, producing ferrocyanide of potassium and hydrated cupric oxide. (Ittner.) In oil of vitriol, which dissolves but little of it, the salt assumes a greenish yellow-white colour; but on subsequent immersion in water, which withdraws the sulphuric acid, it resumes its dark red colour. (Berzelius.)—Insoluble in water and in acids, which do not decompose it; also insoluble in ammoniacal salts. (Brett, Wittstein.)

Cuprous Ferridcyanide. $3Cu^2Cy,Fe^2Cy^3$.—Formed by mixing dichloride of copper dissolved in hydrochloric acid with ferridcyanide of potassium. The red-brown precipitate dissolves instantly in ammonia, but not in its salts. (Wittstein.)

Cupric Ferridcyanide. $3CuCy,Fe^2Cy^3$.—Ferridcyanide of potassium

forms with cupric salts a brownish yellow magma (Gm. Smee); greenish-yellow, according to Williamson. This precipitate contains ferridcyanide of potassium intimately combined. When exposed to sunshine, it becomes brown-red, passing, therefore, into the state of Cu^2FeCy^3.—With aqueous potash, it yields cupric oxide and ferridcyanide of potassium. (Williamson.)—The yellow-green precipitate dissolves immediately in ammonia or carbonate of ammonia, forming a grass-green solution; in other ammoniacal salts, it dissolves partially and only on the application of heat, forming yellow solutions, which become turbid as they cool. (Wittstein.)

Ammonio-ferrocyanide of Copper. — A. *With* 2 *At. Ammonia.* $2NH^3,C^6N^3FeCu^2 = 2NH^3 + Cu^2FeCy^3$. *Cyanoferrure de cuivre ammoniacal.*

1. The ammoniacal solution of cuprous oxide obtained by immersing copper in aqueous ammonia forms, with ferrocyanide of potassium, a pure white, bulky precipitate, which [on exposure to the air] soon changes to a dirty yellow crystalline powder, and when washed with water to which a few drops of hydrochloric acid have been added, is converted into red ferrocyanide of copper. (Grotthuss, *Scher. Ann.* 4, 86.)

2. A cupric salt mixed with ammonia in sufficient quantity to redissolve the precipitate, and then diluted with water, yields with ferrocyanide of potassium, a mixture which becomes olive-green after a while, and afterwards—more quickly at a boiling heat—deposits delicate brown crystalline scales, which after washing, dry up to a yellowish brown, very friable mass, which exhibits but little crystalline structure. This, when heated in a test-tube, becomes first blue, then purple, and afterwards dark coloured, giving off a large quantity of hydrocyanate of ammonia, and yielded reduced copper. Acids withdraw ammonia, and leave dark red ferrocyanide of copper. The compound dissolves in ammonia, but not in water or in alcohol. (Bunsen, *Pogg.* 34, 134.)

3. This compound is also formed by precipitating cupronitrate of ammonia with ferrocyanide of potassium, the reaction being expressed by the equation,

$$2(NH^3,CuO + NH^4O,NO^5) + K^2FeCy^3 = 2(KO,NO^5) + 2NH^3,Cu^2FeCy^3 + 2HO.$$

The pale yellow, crystalline precipitate remains permanent at 100°, but at 130° it begins to give off ammonia, and then yields a sublimate of hydrocyanate of ammonia; when heated in the air, it forms prussian blue. Potash-ley, even at ordinary temperatures, drives off all the ammonia, and forms ferrocyanide of potassium. Concentrated acids eliminate hydrocyanic acid, especially on the application of heat; dilute acids withdraw the ammonia, leaving nothing but ferrocyanide of copper. (Monthiers, *N. J. Pharm.* 11, 249.)

				Bunsen.	Monthiers, at 100°.
6 C	36	16·90			16·81
5 N	70	32·87			32·26
2 Cu	64	30·04		30·33	29·10
Fe	28	13·15		13·20	13·80
7 H	7	3·29			3·27
O	8	3·75			4·76
$2NH^3,C^6N^3FeCu^2 + Aq$	213	100·00			100·00

Monthiers, in analyzing the compound dried in vacuo at ordinary temperatures, found the same composition; Bunsen found 16·14 per

cent. of ammonia in the salt, which he supposes to contain only half as much water as above stated, assigning to it therefore the formula: $2(2NH^3,C^6N^3FeCu^2) + Aq$.

B. *With* 4 *At. Ammonia.* $4NH^3,C^6N^3FeCu^2$. *Cyanoferrure de cuivre biammoniacal.*

1. Ferrocyanide of copper digested with aqueous ammonia diminishes in bulk, and becomes green and crystalline; but if the ammonia be poured off, and water added, the combined ammonia dissolves out, and the red colour is restored. This experiment may be repeated *ad libitum*; the decanted ammonia is pale green, contains but a small quantity of copper in solution, and when mixed with water in closed glass vessels, deposits an orange-yellow substance. (Vauquelin, *Ann. Chim. Phys.* 9, 120; also *Schw.* 25, 60.)

2. Brown-red ferrocyanide of copper, which contains water, absorbs 39·1 p. c. (4 At.) ammoniacal gas, with great rise of temperature and evolution of water, and acquires a fine green colour. Hence the formula: $4NH^3,C^6N^3FeCu^2 + Aq$. The preceding compound B in the dry state does not absorb ammoniacal gas, but in the wet state it absorbs that gas abundantly, with evolution of heat, and likewise turns green. The compound obtained by either of these processes, immediately gives off ammonia when exposed to the air, and recovers its yellow colour. (Monthiers.)

Ferrocyanide of Copper and Potassium. $KCuFeCy^3$.—Formed by dropping a small quantity of a cupric salt, with agitation, into a large quantity of ferrocyanide of potassium. The brown precipitate turns red in a few seconds. It contains no water. It is insoluble in cold water, and when treated with boiling water, gives up part of the ferrocyanide of potassium, together with a trace of the undecomposed compound. (Mosander, *Berzelius, Lehrb.*)

			Mosander.
K	39·2	22·12	20·56
Cu	32·0	18·06	18·47
Fe	28·0	15·80	16·14
3 Cy	78·0	44·02	44·96
C^6N^3FeCuK	177·2	100·00	100·15

Cuprocyanide of Cobalt.—Cuprocyanide of potassium B forms, with cobalt-salts, a precipitate consisting of pale, brown-red, curdy flakes. (Gm.)

Cobaltidcyanide of Copper. $3CuCy,Co^2Cy^3$.—The dense sky-blue precipitate which cobaltidcyanide of potassium forms with cupric salts. (Gm.)—¶ It is also formed by precipitating cupric salts with hydrocobaltidcyanic acid. It is insoluble in water and in acids; warm potash-ley separates cupric oxide from it; ammonia dissolves it completely, forming a blue solution. (Zwenger, *Ann. Pharm.* 62, 170.)

			Zwenger.
2 Co	59·0	41·27	40·75
3 Cu	96·0		
12 C	72·0	19·29	18·70
6 N	84·0	22·54	
7 H	7·0	1·87	2·08
7 O	56·0	15·03	
$Cu^3Co^2Cy^6 + 7Aq$	374·0	100·00	

The 7 At. water contained in this salt appear to be only partially expelled at high temperatures; at 240°, it turns pale green, and gives off 12·94 p. c. (rather more than 5 At.) water. (Zwenger).

Ammonio-cobaltidcyanide of Copper. $2NH^3,Cu^3Co^2Cy^6$.—Crystallizes by slow evaporation from the ammoniacal solution of cobaltidcyanide of copper in small, shining, azure-coloured, four-sided prisms, with octagonal summits; alcohol added to the ammoniacal solution throws down the compound as a blue, slightly crystalline powder of much lighter colour.—The crystals are insoluble in water; when exposed to the air or heated to 100°, they give off ammonia, become opaque, and assume a lighter colour. Acids withdraw the ammonia completely, leaving cobaltidcyanide of copper in the form of a light blue powder. When the compound is heated with potash, ammonia is given off, cupric oxide separated, and cobaltidcyanide of potassium left in solution. (Zwenger, *Ann. Pharm.* 62, 171).

			Zwenger.
2 Co	59	39·74	39·05
3 Cu	96		
8 N	112	28·72	
12 C	72	18·46	18·26
11 H	11	2·82	3·16
5 O	40	10·26	
$2NH^3,C^{12}N^6Co^2Cu^3+5Aq$	390	100·00	

			Zwenger.
$2NH^3$	34	8·72	8·98
3 Cu	96	39·74	
2 Co	59		
6 Cy	156	40·00	
5 HO	45	11·54	
$2NH^3,Cu^3Co^2Cy^6+5Aq$	390	100·00	

The ammonia was determined by decomposing the compound with hydrochloric acid. (Zwenger.) ¶

Cuprocyanide of Nickel.—Cuprocyanide of potassium B added to salts of nickel throws down a greenish white, curdy precipitate (Gm.); bluish green, according to Rammelsberg.

Cyanide of Nickel and Copper.—Cyanide of nickel and potassium forms, with cupric salts, a dense, apple-green precipitate. (Gm.) The precipitate is yellow, gelatinous, and dissolves in ammonia, forming a colourless liquid. (F. & E. Rodgers.)

CYANIDE OF MERCURY. HgCy.—Discovered by Scheele. (*Opusc.* 2, 159.) *Formation.* 1. Heated mercuric oxide absorbs the vapour of hydrocyanic acid, with violent evolution of heat and formation of water; it likewise absorbs hydrocyanic acid vapour very quickly, even when cold. (Gay-Lussac, *Schw.* 16, 31.)—2. Aqueous hydrocyanic acid dissolves mercuric oxide with a rise of temperature, which, if the acid be somewhat concentrated, may amount to explosion; even dilute hydrocyanic acid becomes strongly heated by contact with mercuric oxide. (Gay-Lussac.)—3. Mercuric oxide, even when combined with nitric and other acids, converts hydrocyanic acid into cyanide of mercury, with separation of nitric acid, &c.—4. With mercurous oxide, mercurous nitrate, or calomel, hydrocyanic forms cyanide of mercury, metallic

mercury, and water, with separation of nitric or hydrochloric acid (Scheele):

$$HCy + Hg^2O = HgCy + Hg + HO.$$

Respecting the formation of cyanide of mercury from calomel, *vid.* VI, 49, 50. Cyanide of potassium with mercurous nitrate, yields cyanide of mercury, metallic mercury, and nitrate of potash. (Scheele).—5. Mercuric oxide placed in contact with the cyanides of any of the other metals (excepting cyanide of palladium), yields cyanide of mercury and an oxide of the other metal (Proust, *N. Gehl.* 3, 582,) *e. g.* with cyanide of potassium:

$$HgO + KCy = HgCy + KO.$$

Even the metallic prussides, such as prussian blue and the red and yellow prussiates of potash, yield cyanide of mercury when treated with mercuric oxide.

Preparation. 1. Finely pulverized mercuric oxide is added with agitation to dilute hydrocyanic acid in a close vessel, till the odour of the acid is destroyed,—after which the filtrate is evaporated to the crystallizing point. If the solution of the oxide be ultimately aided by heat, the acid may take up an excess of it; in that case, hydrocyanic acid must be added, with agitation, till the liquid no longer reddens turmeric, and again begins to smell of hydrocyanic acid. This mode of preparation, first recommended by Schrader (*Repert.* 12, 122), afterwards by Winckler (*Repert.* 31, 471), Chevallier & Deleschamps (*J. Chim. méd.* 6, 35), Martius (*Repert.* 41, 209), and others, yields the purest preparation.

2. Mercuric oxide is heated with about an equal weight of finely pounded prussian blue, and a large quantity of water, the mixture being frequently stirred (Scheele); and the filtrate is boiled with mercuric oxide to throw down the last portions of iron (Proust); whereupon the excess of mercuric oxide in the filtrate is neutralized with hydrocyanic acid. (Gay-Lussac.)—The prussian blue must either be prepared specially for the purpose, or it must be freed from ferric oxide and alumina, by boiling in hydrochloric acid and washing with water; otherwise the filtrate will be yellow, and will contain a large quantity of iron.—8 parts of purified prussian blue require 11 parts of mercuric oxide; if 12 parts of mercuric oxide be used, the filtrate will be alkaline from excess of that oxide, and will be coloured by ferric oxide, which will be deposited during the evaporation of the liquid; but with 11 pts. of mercuric oxide, a colourless filtrate is obtained. (Turner, *Edinb. J. of Sc.* 5, 245).—According to Proust and Gay-Lussac, on the contrary, all the ferric oxide is separated by excess of mercuric oxide; but if the quantity of mercuric oxide be deficient, ferric oxide passes into the solution. Ittner had previously shown that when prussian blue is boiled with a quantity of mercuric oxide, not sufficient for its complete conversion, a ferruginous filtrate is obtained, from which yellowish prisms crystallize; that the whole of the iron contained in this filtrate may be removed by continued boiling with mercuric oxide; and that hydrochloric acid added to it throws down about 10 parts of protocyanide of iron. This ferruginous filtrate may be completely freed from iron by mere evaporation to dryness; the dry residue dissolved in water, yields a colourless filtrate free from iron. (*Pogg.* 24, 365.)—If we take as the basis of the calculation, the analyses of prussian blue made by Berzelius and Williamson, it will appear that 100 pts. of prussian blue require from 172 to 164 pts. of mercuric oxide; but as prussian blue rarely exhibits the degree of

purity and dryness which this calculation supposes, the quantity of mercuric oxide actually required is somewhat less, and must be determined by trial. The boiling must be continued till a portion of the solid matter at the bottom of the liquid gives only a brown streak when triturated; if a blue streak still appears after long boiling, more mercuric oxide must be added; a yellow streak, on the contrary, indicates a deficiency of prussian blue. (Gm.)—Ferrocyanide of potassium, which often occurs in prussian blue, dissolves together with the cyanide of mercury, and causes the crystals of that substance to be mixed with crystals of a compound which it forms with ferrocyanide of potassium. Robiquet, *Ann. Chim. Phys.* 44, 279.)

3. One pt. of ferrocyanide of potassium is boiled for 10 minutes with 2 pts. of monobasic mercuric sulphate (freed by strong heating from excess of sulphuric acid) and 8 pts. of water, the liquid filtered from the scanty whitish sediment, and left to cool till the cyanide of mercury crystallizes. (Desfosses, *J. Chim. méd.* 6, 261.) The theory of this process, according to which 100 pts. of ferrocyanide require 245 pts. of mercuric sulphate, and should yield 179 pts. of cyanide of mercury, has been already given (VII. 465, 466). If the undissolved matter is blue, a small additional quantity of mercuric sulphate must be added before filtering, and the liquid boiled, till the solid matter becomes white or greenish white. The crystals obtained on cooling amount to 1 pt. for every 1 pt. of ferrocyanide of potassium. The mother-liquor, which likewise contains sulphate of potash [and ferric sulphate], if decanted, evaporated to a pasty consistence, and then well boiled with alcohol—which must be removed by straining through linen—will yield from 0·25 to 0·3 pt. more of impure cyanide of mercury. The crystals thus obtained may be purified by recrystallization. (Desfosses.) Geiger (*Mag. Pharm.* 34, 133), and Liebig (*Pogg.* 24, 365, recommend only 1 pt. of mercuric sulphate to 1 pt. of ferrocyanide of potassium. But even with 1 pt. of ferrocyanide to 1·4 pt. of the mercury salt, only the cyanide of potassium in the ferrocyanide is decomposed, the cyanide of iron remaining in the form of a powder which turns blue in the air. Ferrocyanide of barium obtained by decomposing prussian blue with aqueous sulphide of barium, is preferable to ferrocyanide of potassium, because it obviates the contamination of the product with sulphate of potash; still better is ferrocyanide of lead, obtained by precipitating acetate or nitrate of lead with ferrocyanide of potassium. (Duflos, *Schw.* 65, 112 and 235).

Properties. Colourless square prisms, sometimes transparent, sometimes clouded. *Fig.* 34, $q : q = 90°$; $q : a = 132° 45'$; $q : e = 112° 40'$; $e : e' = 114°$. Sometimes merely square prisms bevelled with two a-faces at top, and with other a-faces oppositely situated at bottom. (Brooke, *Ann. Phil.* 22, 43.) The author obtained the same form; but of the four a-faces at the completely formed extremity, only two opposite ones were present. The salt has a bitter, metallic taste, and exhibits the poisonous properties of hydrocyanic acid combined with those of corrosive sublimate:

			Gay Lussac.	Parrett.	Johnston.
Hg	100	79·37	79·91	79·08	
Cy	26	20·63	20·09		20·73
HgCy	126	100·00	100·00		

Decompositions. 1. Cyanide of mercury, when *heated*, turns black,

softens, and yields, if perfectly dry, nothing but cyanogen gas and mercury; part of the cyanogen is, however, resolved into nitrogen gas [?], and a very light nitrogenous charcoal [paracyanogen], which like cyanogen contains 2C to 1N, the quantity thus decomposed being greater as the heat is stronger; at the same time, a small quantity of cyanide of mercury sublimes undecomposed. If, on the other hand, the cyanide of mercury is moist, it yields carbonic acid, ammonia, hydrocyanic acid and mercury. (Gay-Lussac.)—100 grains, HgCy, should yield 37·642 cubic inches of cyanogen gas; but the quantity actually obtained is only 30·92 cub. in., because paracyanogen is likewise formed, which contains the C and N of the deficient cyanogen in the same proportion as the cyanogen itself. (Johnston, *N. Ed. of Sc.* 1, 110; also *Schw.* 57, 375.)—According to Scheele, cyanide of mercury is decomposed by heat into mercury, hydrocyanic acid, and a small quantity of ammonia, part of the original substance, however, subliming undecomposed.

2. Dry cyanide of mercury is not decomposed by dry *chlorine gas* in the dark; but in strong sunshine it undergoes decomposition, emitting the odour of chloride of cyanogen (Gay-Lussac), and in 10 days, yields protochloride of mercury and a yellow oily liquid (*vid. Oil of Chloride of Cyanogen*). Serullas (*Ann. Chim. Phys.* 35, 293).—Cyanide of mercury exposed in the moist state to chlorine gas, is converted in the dark into protochloride of mercury and volatile chloride of cyanogen (Serullas):

$$HgCy + 2Cl = HgCl + CyCl.$$

But in strong sunshine,—its temperature rising to 30° or 40°,—it yields sal-ammoniac, protochloride of mercury, the above-mentioned yellow oil, a small quantity of volatile chloride of cyanogen, and a trace of carbonic acid. If the cyanide of mercury be completely dissolved in water, chlorine in sunshine produces a large quantity of the yellow oil and a small quantity of volatile chloride of cyanogen. (Serullas).—¶ According to Bouis (*N. Ann. Chim. Phys.* 20, 446; *Jahresber*, 1847–8, 486), a hot saturated solution of cyanide of mercury treated with excess of chlorine in sunshine, is converted into chloride of mercury, hydrochloric acid, and sal-ammoniac, which remain dissolved in the water, chloride of cyanogen, carbonic acid, and nitrogen, which escape, and a yellow, oily liquid, to which Bouis assigns the formula $C^{12}N^4Cl^{14}$. ¶—A mixture of the aqueous solutions of cyanide of mercury and chloride of lime, which is clear at first, begins in a few minutes to emit white fumes, effervescing violently and giving off nitrogen, carbonic acid, and a small quantity of cyanogen; neither cyanic nor cyanuric acid is produced in this reaction. (Liebig, *Pogg.* 15, 571.)—3. *Bromine* at medium temperatures decomposes cyanide of mercury, with great evolution of heat, yielding protobromide of mercury and bromide of cyanogen. (Serullas, *Ann. Chim. Phys.* 31, 100.)—4. *Iodine*, even when triturated cold with cyanide of mercury, yields protodide of mercury and iodide of cyanogen. (H. Davy, Porrett).

5. When cyanide of mercury is distilled with ⅓ of its weight of *Sulphur*, the mass fuses, gives off nitrogen, cyanogen, and vapour of sulphide of carbon; becomes viscid, swells up, and leaves a black mass insoluble in water; and this, when further heated, yields nitrogen, cyanogen, sulphide of carbon, and cinnabar, while light yellow disulphocyanide of mercury remains, which at a higher temperature gently sublimes in the form of a yellow, sometimes translucent, crystalline mass, but is for the most part resolved into cyanogen gas and cinnabar. (Berzelius, *Schw.* 31, 58.) Hence the sulphur, with half the cyanogen, forms disulphocyanide of

mercury; the other half of the cyanogen escapes partly undecomposed, partly resolved into nitrogen and sulphide of carbon; if the heat be continued, the disulphocyanide of mercury is resolved into cyanogen gas and cinnabar. (Berzelius). On the action of *Phosphorus* on cyanide of mercury, *vid.* Cenedella (*J. Pharm.* 21, 683.) — 6. Cyanide of mercury forms with *oil of vitriol* a pasty mass, which smells faintly of hydrocyanic acid, and if the oil of vitriol is in excess, assumes a yellow colour, probably from some decomposition of the hydrocyanic acid. Water added to this compound separates part of the cyanide of mercury, dissolving the remainder together with the sulphuric acid; a larger quantity of water dissolves the whole. (Berzelius). When cyanide of mercury is heated with oil of vitriol, sulphurous acid is formed. (Proust, Ittner.) This reaction likewise produces carbonic acid gas, sulphate of ammonia, and sulphate of mercury. (Berzelius, *Lehrb.*) When cyanide of mercury is boiled with dilute sulphuric acid, an evolution of gas takes place, and mercurous sulphate is precipitated in the form of a white powder. (Mohr. *Ann. Pharm.* 31, 187.) Dilute sulphuric acid does not liberate hydrocyanic acid from cyanide of mercury, even when heated with it; even boiling nitric acid exerts no decomposing action. (Proust, *N. Ann. Chim. Phys.* 3, 582.) — 7. The *hydrogen-acids* decompose cyanide of mercury, yielding hydrocyanic acid, and a compound of mercury with the radical of the acid in equal numbers of atoms. Thus: hydrosulphuric acid yields hydrocyanic acid and protosulphide of mercury; hydriodic acid: hydrocyanic acid and protoiodide of mercury; hydrochloric acid: hydrochloric acid and protochloride of mercury. An excess of hydrochloric acid, aided by heat, may convert the resulting hydrocyanic acid into ammonia and formic acid; in that case, the residue will be a compound of corrosive sublimate and sal-ammoniac. — 8. Cyanide of mercury heated with excess of *sal-ammoniac* and with water, is resolved into hydrocyanate of ammonia, and a compound of corrosive sublimate and sal-ammoniac. (Duflos.) If the numbers of atoms of the two compounds be equal, the dry mixture fuses and is resolved into hydrocyanate of ammonia and corrosive sublimate (Bineau, *Ann. Chim. Phys.* 67, 231):

$$HgCy + NH^4Cl = HgCl + NH^4Cy.$$

9. Aqueous *protochloride of tin* decomposes cyanide of mercury, giving off hydrocyanic acid (Proust), and precipitating a black mixture of stannic oxide and mercury. (A. Vögel, *Kastn. Arch.* 23, 81; Poggiale, *Compt. rend.* 23, 762):

$$2HgCy + 2\,SnCl + 2HO = 2Hg + 2HCy + SnCl^2 + SnO^2.$$

10. *Iron filings* and dilute sulphuric acid repeatedly agitated with cyanide of mercury decompose it, yielding hydrochloric acid, metallic mercury, and ferrous sulphate (Scheele):

$$HgCy + Fe + HO + SO^3 = Hg + HCy + FeO,SO^3.$$

Iron filings without sulphuric acid, and without access of air, reduce the mercury, and yield protocyanide of iron. (Simon, *Scher. J.* 8, 47.) An iron plate immersed in an aqueous solution of cyanide of mercury which is exposed to the air, causes a gradual evolution of hydrocyanic acid and separation of mercury, while the plate itself becomes covered with hydrated ferric oxide, and here and there also with prussian blue. (Guibourt, *J. Chim. méd.* 14, 187.)—11. Aqueous *persulphide of potassium*

decomposes cyanide of mercury, yielding sulphide of mercury and sulphocyanide of potassium (Porrett, Duflos, *Schw.* 65, 238.)

$$HgCy + KS^3 = HgS + KCyS^2.$$

Aqueous *alkalies* exert no decomposing action even on boiling. (Scheele).

Cyanide of mercury dissolves with tolerable facility in water, less easily in hydrated alcohol, and is nearly insoluble in absolute alcohol.

Oxycyanide of Mercury. HgCy,HgO.—First obtained by Proust. (*Ann. Chim.* 60, 228; also *N. Gehl*, 3, 581.)—1. A concentrated solution of cyanide of mercury is boiled with mercuric oxide, filtered hot, and left to crystallize by cooling. (Proust, Gay-Lussac.)—2. Aqueous hydrocyanic acid, containing from 10 to 20 per cent. of the anhydrous acid, is mixed with an excess of pulverized mercuric oxide, whereupon a considerable quantity of the white compound becomes mixed with the oxide; the whole is then washed on a filter with boiling water, and the filtrate left to cool, till it crystallizes. (Johnston, *Phil. Transact.* 1839, 113.)

White, four-sided needles, united in tufts. In the state of aqueous solution, the compound has an alkaline reaction. (Proust, Gay-Lussac, Johnston.) Sulphur-yellow. (H. Schlieper.)

			Johnston.	Schlieper.
2 Hg	200	85·47	85·68	85·14
2 C	12	5·13	5·20	5·99
N	14	5·98	6·02	5·15
O	8	3·42	3·10	3·72
HgCy,HgO	234	100·00	100·00	100·00

According to Grouvelle, the compound = 3HgCy,2HgO. According to Kühn (*Schw.* 61, 240), 378 pts. (3 At.) of cyanide of mercury dissolved in water and boiled for some time with excess of mercuric oxide take up only 107·1 (not quite 1 At.) of the oxide. [Perhaps the solution was too dilute.]

The dry crystals, heated for some time to 100°, turn grey, from formation of a mercurous salt. (Schlieper.) At a somewhat higher temperature, they blacken, and then yield carbonic acid, cyanogen, and nitrogen gas, besides mercury. (Gay-Lussac, *Pogg.* 53, 141.) This decomposition is accompanied by a tolerably strong detonation, but the compound does not detonate under the hammer. (Johnston, Schlieper, *Ann. Pharm.* 59, 10.)—The moist crystals, when heated, give off carbonic oxide, carbonic acid, hydrocyanic acid, ammonia, an oil, and mercury, and leave a small quantity of carbonaceous matter (paracyanogen). (Proust.)—The powder of the crystals, heated for some time under water, is converted, by partial decomposition, into a yellow powder, mixed with a small quantity of mercury. (Johnston.)—Warm hydrochloric acid dissolves the compound with evolution of hydrocyanic acid, and forms protochloride of mercury. (Johnston.) The compound dissolves readily in strong sulphuric acid; water added to the solution throws down trisulphate of mercuric oxide, and retains cyanide of mercury in solution. (Schlieper.)—Very dilute nitric acid neutralized with the compound, leaves, on evaporation, a crystalline compound of cyanide of mercury with mercuric nitrate. (*Vid. inf.*)—A similar compound is formed by acetic acid. (*Vid. inf.*)—Nitrate of silver yields a compound of cyanide of mercury with itself (*q.v.*)—Ammonia throws down from the cold aqueous solution a thick white precipitate, and from the hot solution a yellowish precipitate of hydrated mercurate of ammonia, while cyanide of mercury

remains in the solution. (Johnston.)—Sal-ammoniac renders the solution strongly alkaline, and throws down *white precipitate.* Probably thus:

$$2(HgCy,HgO) + 2NH^4Cl = 2HgCy + HgCl,HgNH^2 + NH^4Cl + 2HO.$$

The precipitate redissolves on boiling, the liquid at the same time giving off ammonia, and losing its alkaline reaction.—Chloride of potassium and chloride of sodium render the solution more strongly alkaline, by forming protochloride of mercury and alkali, and yield a small white precipitate. The crystals dissolve abundantly in boiling aqueous solution of chloride of potassium, and the liquid, on cooling, deposits scales of KCl,HgCy, while potash and protochloride of mercury remain in solution. (Johnston.) [Can potash and protochloride of mercury exist in solution together?] The aqueous solution of iodide or cyanide of potassium yields similar scales. (Johnston.)

The compound dissolves very sparingly in cold water, but with tolerable facility in boiling water. (Schlieper.) It is soluble to a certain extent in hydrated alcohol. (Kühn.)

According to Schrader (*Berl. Jahrb.* 1821, 91,) there exists another oxycyanide of mercury, richer in oxygen and insoluble in water.

Chlorocyanide of Mercury. HgCl,HgCy.—The mixture of the aqueous solutions of the two compounds evaporated to a certain point, solidifies, on cooling, into a white crystalline mass, which liquefies again when gently heated, and dissolves readily in water. (Liebig, *Schw.* 49, 253.)—Translucent, four-sided pyramids, permanent in the air. Their aqueous solution added to nitrate of silver throws down nothing but chloride. (Poggiale, *Compt. rend.* 23, 762.)—Carbonate of potash forms with the solution a yellow precipitate, which dissolves in acids without effervescence, but with evolution of hydrocyanic acid. (Liebig.)

Cyanide of Mercury with Mercuric Nitrate.—When very dilute nitric acid is saturated with oxycyanide of mercury, till it no longer reddens litmus, the liquid yields, by evaporation, transparent, colourless, slender four-sided prisms, six-sided tables, or nacreous scales. These crystals lose nothing at 100°; when more strongly heated in a tube, they detonate slightly, and give off nitrous vapours. Heated in the air, they decompose with a white light, giving off vapour of mercury, and leaving a yellow residue. They dissolve readily in water. Since 234 pts. (1 At.) of oxycyanide of mercury yield 247·4 pts. of these crystals, it is evident that $\frac{1}{4}$ At. of nitric acid must have entered into their composition. (Johnston.)

Cyanide of Mercury with Ammonia.—126 pts. of cyanide of mercury absorb very slowly 9·954 pts. of ammonia; in a longer time they take up more, and ultimately perhaps 17 pts. (1 At.) The compound gives off its ammonia at a temperature not sufficient to decompose the cyanide of mercury. It forms a clear solution in water. (H. Rose, *Pogg.* 20, 161.)

Cyanide of Mercury with Chloride of Ammonium. $NH^4Cl,2HgCy$.—The aqueous solution of 13 pts. sal-ammoniac and 60 pts. cyanide of mercury yields, on evaporation, four-sided needles, which, after drying, have a somewhat silky lustre. (Brett, *Phil. Mag. J.* 12, 235; abstr. *J. pr. Chem.* 14, 118.)—Long needles having a mercurial taste. (Poggiale, *Compt. rend.* 23, 762.)—The crystals become opaque by exposure to the air. (Poggiale.)—They fuse when heated, and decompose with evolution

of ammonia and hydrocyanic acid (Brett), of carbonic acid, cyanogen, mercury, and sal-ammoniac. (Poggiale.)—When more strongly heated with oil of vitriol, they give off cyanogen, sulphurous acid, carbonic acid, and hydrochloric acid. (Poggiale.)—Mineral acids do not decompose them at ordinary temperatures, but decomposition ensues on the application of heat. (Brett.)—They are soluble in water and in alcohol. (Brett.)

			Brett.
NH^4Cl	53·4	17·49	16·8
2 HgCy	252·0	82·51	79·4
$NH^4Cl,2HgCy$	305·4	100·00	96·2

Brett attributes the loss in his analysis to hygroscopic water.—Poggiale likewise mentions a salt, $2NH^4Cl,HgCy$, which separates on evaporation from the mother-liquid of the preceding salt, in triangular laminæ.

Cyanide of Mercury and Potassium.—KCy,HgCy.—Obtained by dissolving cyanide of mercury in aqueous cyanide of potassium, and evaporating the solution till it crystallizes. (Gm. *Handb.* Aufl. 2, 2, 1693.) Cyanide of mercury treated with hydrocyanic acid and carbonate of potash likewise yields this compound, its formation being accompanied by slow evolution of carbonic acid; it is also formed by treating mercuric oxide with aqueous cyanide of potassium, potash being produced at the same time. (Gm.)—Sulphide of mercury does not dissolve in aqueous cyanide of potassium. (Haidlen & Fresenius.)

Colourless, transparent, or translucent regular octohedrons, generally in the form of segments; they are permanent in the air. (Gm.)

	Crystallized.		Rammelsberg.	Gm.
K	39·2	20·50	19·22	20·73
Hg	100·0	52·30	54·20	51·18
2 Cy	52·0	27·20		
KCy,HgCy	191·2	100·00		

Rammelsberg dried the crystals, previous to analysis, at 150°, at which temperature they gave off merely a trace of hygroscopic water.—According to Jackson (*Thomson's Records of gen. Sc.* 1836; also *Berz. Jahresber.* 17, 181), who regards himself as the discoverer of this salt, it contains 9·3 per cent. (1 At.) KCy to 91·0 per cent. (5 At.) HgCy.

The salt decrepitates violently when heated, and afterwards melts into a brown liquid, which gives off cyanogen gas and vapour of mercury. Sulphuretted hydrogen passed through the solution of the salt throws down all the mercury in the form of sulphide. (Gm.)—Hydrochloric acid expels all the hydrocyanic acid; nitric acid [sulphuric or acetic; Gm.], only that portion which proceeds from the cyanide of potassium. Alkalis exert no action upon it. The solution added to cupric salts throws down yellow protocyanide of copper. (Rammelsberg, *Pogg.* 38, 374, and 42, 131.)—With various metallic salts, it forms the following precipitates, the odour of hydrocyanic acid being at the same time evolved: lead-salts, white; green vitriol, bluish white; sesquichloride of iron, yellowish brown; mercurous nitrate, grey (metallic mercury), but without the odour of hydrocyanic acid; with nitrate of silver it yields white cyanide of silver. (Gm.)—The salt dissolves in 4·4 pts. of cold water, forming a solution which smells faintly of hydrocyanic acid. (Gm.)

Comp. Meillet (*N. J. Pharm.* 3, 443), who likewise regards himself as the discoverer of this compound.—By boiling ferrocyanide of potassium with aqua-regia, mercuric oxide, and water, and cooling the filtrate, Desfosses (*J. Chim. méd.* 6, 261,) obtained white crystalline scales, probably consisting of KCy,HgCy,2Aq.

¶ *Cyanide of Mercury with Hyposulphite of Potash.* KO,S^2O^2+HgCy.—Obtained in the form of large four-sided prisms, by mixing a solution of 1 At. hyposulphite of potash with a solution of 1 At. cyanide of mercury, adding a small quantity of alcohol, and concentrating the mother-liquid in vacuo. (Kessler, *Pogg.* 74, 274.) ¶

Cyanide of Mercury with Iodide of Potassium. KI,2HgCy.—1. A mixture of the aqueous solutions of cyanide of mercury and iodide of potassium deposits these crystals, which may be purified by washing with cold water and recrystallization. (Caillot, *Ann. Chim. Phys.* 19, 220; also *N. Tr.* 6, 2, 273; abstr. *Schw.* 49, 253.)—2. The solution of iodide of mercury in boiling aqueous cyanide of potassium yields the same crystals, on cooling. (Souville, *J. Pharm.* 26, 476.)—Winckler (*Br. Arch.* 8, 83) likewise obtained them by mixing hydrocyanic acid containing cyanide of mercury, with iodine, and adding potash till the precipitated iodide of mercury was redissolved.—3. By boiling protiodide of mercury with ferrocyanide of potassium and water, filtering from the cyanide of iron, and cooling. (Preuss, *Ann. Pharm.* 29, 325; Souville.)

Large, soft, white laminæ, which have a pearly lustre, are permanent in the air, inodorous in the dry state, but smell of hydrocyanic acid when moist. (Caillot.)—They have a silvery lustre. (Liebig.) Four-sided needles having a pearly lustre. (Apjohn, *Phil. Mag. Ann.* 9, 401. Long, white, shining needles, having a very unpleasant, sour taste. (Souville.)

Crystallized.			Liebig.	Apjohn.	Caillot.*
KI	165·2	39·60	39·42	38·68	
2 HgCy	252·0	60·40		60·40	58·82
KI,2HgCy	417·2	100·00		99·08	

* Inasmuch as, according to Caillot, sulphuretted hydrogen throws down 54·167 parts of cyanide of mercury from 100 parts of the salt.

The crystals, when moderately heated (to 120°), do not diminish in weight; at a higher temperature, they give off cyanogen, mercury, and mercurous iodide, and leave a residue of iodide of potassium, blackened with a small quantity of charcoal. (Caillot.) They give off first cyanogen, then mercury, and leave iodide of potassium. (Liebig.) They fuse, give off mercury, iodide of mercury, and a small quantity of undecomposed cyanogen, while the greater portion of the cyanogen is decomposed, so that cyanide of potassium is left mixed with charcoal. (Souville.) Chlorine forms, with the solution, a red precipitate, soluble in excess of the solution. (Caillot.) Chlorine gas, chlorine-water, bromine, nitrous acid, and fuming nitric acid, blacken the crystals, by separating iodine. (Bailley, *Sill. Amer. J.* 31, 85; also *J. pr. Chem.* 12, 56.) Most acids, even arsenious and benzoic (but not carbonic or hydrocyanic acid) throw down from the solution a red precipitate of iodide of mercury, a potash-salt being formed, and hydrocyanic acid evolved at the same time. If sulphuric acid be used somewhat in excess, part of the cyanide of mercury remains dissolved in the liquid (Caillot):

$$KI,2HgCy + SO^3 + HO = KO,SO^3 + HCy + HgI + HgCy.$$

Hence the crystals are reddened by immersion in the aqueous solution of hydrochloric, sulphuric, phosphoric, hydrofluoric, chromic, acetic, oxalic, tartaric, or citric acid. (Bailey.)—From lead-salts the solution throws down yellow iodide of lead, and from mercuric salts, red iodide of mercury.

(Caillot.)—Hydrosulphuric acid and alkaline hydrosulphates throw down black sulphide of mercury. Ammonia, potash, and soda, exert no decomposing action. (Caillot.)—The crystals dissolve in 16 parts of cold water, and in a smaller quantity of hot water; the more concentrated the solution thus formed, the greater is the quantity of iodine that it will take up. (Caillot.) When heated, it takes up mercuric iodide, which separates out again on cooling. (Souville.—The crystals dissolve in 96 parts of cold alcohol of 34° Bm. (Caillot), and are slightly soluble in ether (Souville.).

Cyanide of Mercury with Bromide of Potassium. KBr,2HgCy.—On mixing the aqueous solutions of cyanide of mercury and bromide of potassium, this compound is immediately precipitated in white scales, which may be collected on a filter, washed, and purified by recrystallization. (Caillot, *J. Pharm.* 17, 351.)—Better crystals are obtained by mixing the solutions in the dilute state, so that they may not form an immediate precipitate, and subsequently evaporating and cooling the mixture. (Brett, *Phil. Mag. J.* 11, 340; also *J. pr. Chem.* 12, 430.)—Broad, thin, white, nacreous laminæ, having a mercurial taste. (Caillot.) By slow crystallization delicate four-sided needles are produced. (Brett.)

Dried by heat.			Caillot.	Brett.
KBr	119·2	32·11	31·3	31·34
2 HgCy	252·0	67·89	68·3	62·87
KBr,2HgCy	371·2	100·00	99·6	94·21

The crystals contain 8·74 per cent. (2 At.) of water. (Caillot.)

The salt, when ignited in a covered crucible, leaves a mixture of bromide of potassium, cyanide of potassium, and charcoal. (Caillot.) During the decomposition, the salt first melts and afterwards blackens. (Brett.) Dilute nitric acid decomposes it, yielding hydrocyanic acid, nitrate of potash, protobromide of mercury, and cyanide of mercury; hence the mixture, if heated with common salt, again gives off hydrocyanic acid. (Caillot.) Nitric acid does not decompose the salt, even with the aid of heat, at least not immediately. (Brett.) Sulphuretted hydrogen and sulphide of potassium throw down sulphide of mercury from the solution. (Caillot.) Protochloride of tin boiled with the solution eliminates hydrocyanic acid, and precipitates mercury. (Brett.) Aqueous solution of potash or soda exerts no decomposing action. (Brett.) From the salts of the alkaloids, those of cinchonine for example, the solution throws down a compound of a hydrobromate of the alkaloid with cyanide of mercury. (Caillot.)

The salt dissolves in 13·34 pts. of water at 18°, and in less than 1 pt. of boiling water. (Brett.) It dissolves in dilute sulphuric acid, without being decomposed, even on boiling; it likewise dissolves without decomposition in hot oil of vitriol, and is not precipitated from the solution by water. It also dissolves without decomposition in nitric acid, whether cold or hot, dilute or concentrated; also in hydrochloric acid, forming a solution which is not decomposed even by heat. (Brett.) It dissolves in alcohol, especially when hot. (Caillot, Brett.)

Cyanide of Mercury with Chloride of Potassium. KCl,2HgCy.—1. Formed by mixing the aqueous solutions of cyanide of potassium and chloride of mercury (Desfosses, *J. chim. méd.* 6, 261), or of chloride of potassium and cyanide of mercury. (Brett, *Phil. Mag. J.* 11, 342; also

J. pr. Chem. 12, 433.)—2. Aqueous ferrocyanide of potassium boiled with corrosive sublimate, filtered, and cooled, yields the same crystals. (Desfosses.) White crystalline laminæ. (Desfosses.) In its properties and chemical relations, it resembles the compound of cyanide of mercury with bromide of potassium. (Brett.) The crystals, when heated, fuse in their water of crystallization, then give off cyanogen, and leave chloride of potassium mixed with a small quantity of carbonate of potash. (Desfosses.) The aqueous solution is decomposed by sulphuretted hydrogen, sulphide of potassium, and protochloride of tin, but not by acids or alkalis. (Brett.) The salt dissolves in 6·75 parts of water at 18° (Brett); it is also soluble in alcohol. (Desfosses.)

Crystallized.			Desfosses.	Brett.
KCl	74·6	22·23	22·0	22·67
2 HgCy	252·0	75·09	74·4	72·07
Aq	9·0	2·68	2·6	
KCl,2HgCy + Aq	335·6	100·00	99·0	

Cyanide of Mercury and Sodium.—Octohedrons. (*Berzelius, Lehrb.*)

¶ *Cyanide of Mercury with Iodide of Sodium.* NaI,2HgCy + 4Aq.—Four-sided prisms, having a silky lustre. They give off all their water at 210°; are easily soluble in water and alcohol; and are decomposed by mineral acids, with evolution of hydrocyanic acid and precipitation of mercuric iodide. (Custer, *Arch. Pharm.* [2], 56, 1; *Pharm. Centr.* 1849, 3; *Chem. Gaz.* 1849, 101; *Jahresber.* 1847—8, 477.) ¶

Cyanide of Mercury with Bromide of Sodium. NaBr,2HgCy.—Formed by dissolving 1 At. bromide of sodium, together with 2 At. cyanide of mercury, in water, and leaving the solution to crystallize. The long flat needles, which have a silvery lustre, are permanent in moist air; but when exposed to a dry atmosphere, lose their water of crystallization, and with it their lustre. They are decomposed by acids and by the salts of the alkaloids. They dissolve very readily in water and in alcohol. (Caillot, *J. Pharm.* 17, 351.)

Crystallized.			Caillot.
NaBr	103·2	27·00	26·48
2 HgCy	252·0	65·93	66·59
3 Aq	27·0	7·07	6·93
NaBr,2HgCy + 3Aq	382·2	100·00	100·00

Cyanide of Mercury with Chloride of Sodium. NaCl,2HgCy.—The aqueous solution of 1 pt. common salt and 4 pts. cyanide of mercury yields on evaporation, flat four-sided prisms, having a faint silky lustre, and soluble in water and dilute alcohol. (Brett, *Phil. Mag. J.* 12, 235.) Transparent needles which contain no water of crystallization, dissolve readily in water, especially when hot, and are sparingly soluble in alcohol. (Poggiale, *Compt. rend.* 23, 762.)

			Brett.
NaCl	58·6	18·87	17·8
2 HgCy	252·0	81·13	79·4
NaCl,2HgCy	310·6	100·00	97·2

Respecting the reactions of cyanide of mercury dissolved in solution of common salt and sal-ammoniac, *vid.* Mialhe, (*N. Ann. Chim. Phys.* 5, 181).

¶ *Cyanide of Mercury with Iodide of Barium.* BaI,2HgCy + 4Aq.—Crystallizes in square tables, and in other respectsrese mbles the sodium salt. (Custer.) ¶

Cyanide of Mercury with Bromide of Barium. BaBr,2HgCy.—Crystallizes from the aqueous solution of 3 pts. bromide of barium and 5 pts. cyanide of mercury in thin, very shining square laminæ. These crystals lose their lustre on exposure to dry air, and when heated nearly to the point at which they decompose, give off 11·8 p. c. water. They dissolve in hot water and alcohol, more readily than in the same liquids when cold. Their solution is precipitated by sulphuretted hydrogen, sulphuric acid, and the salts of the alkaloids. (Caillot, *J. Pharm.* 17, 351.)

	Crystallized.		Caillot.
BaBr	148·6	32·69	32·19
2 HgCy	252·0	55·43	55·98
6 Aq	54·0	11·88	11·83
BaBr,2HgCy + 6Aq	454·6	100·00	100·00

Cyanide of Mercury with Chloride of Barium. BaCl,2HgCy.—The solution of 2 pts. chloride of barium and 5 pts. cyanide of mercury in water, yields on evaporation flat, four-sided prisms, easily soluble in water and weak alcohol. Sulphuric acid added to them, throws down the baryta. (Brett.) With 4 At. water, the salt crystallizes in oblique four-sided prisms, which are efflorescent, give off their water when heated, and are subsequently resolved into cyanogen gas, vapour of mercury, and chloride of barium. They are precipitated by sulphuretted hydrogen, and likewise by carbonates and sulphates. (Poggiale.)

			Brett.
BaCl	104	29·21	28·0
2 HgCy	252	70·79	70·7
BaCl,2HgCy	356	100·00	98·7

¶ *Cyanide of Mercury with Iodide of Strontium.* SrI,2HgCy + 6Aq.—Similar to the corresponding barium-salt. (Custer.) ¶

Cyanide of Mercury with Bromide of Strontium. SrBr,2HgCy.—Colourless rhombic laminæ, which effloresce in the air, but do not give off all their water till heated nearly to the point at which they decompose. The salt dissolves in water and alcohol; gives off hydrocyanic acid when treated with stronger acids; and is decomposed by alkaline carbonates. (Caillot.)

	Dehydrated.		Caillot.
SrBr	124	28·84	28·55
2 HgCy	252	58·60	
6 Aq	54	12·56	
SrBr,2HgCy + 6Aq	430	100·00	

Cyanide of Mercury with Chloride of Strontium. SrCl,2HgCy.—Crystallizes from the aqueous solution of 19 pts. chloride of strontium and 60 pts. cyanide of mercury, in long, flat, four-sided prisms, having a silvery lustre, easily soluble in water and in weak alcohol. (Brett.) Silky needles, which contain 6 At. water, become dull by exposure to the air, dissolve very readily in water, and are decomposed by sulphuretted hydrogen, sulphates and carbonates. (Poggiale.)

					Brett.
SrCl	79·4	....	23·96	.....	23·7
2 HgCy	252·0	....	76·04	.....	75·5
SrCl,2HgCy	331·4	....	100·00	.....	99·2

Cyanide of Mercury with Iodide of Calcium. CaI,2HgCy.—This salt, with 6 At. water, yields silky, crystalline tufts, which are slightly efflorescent, and very soluble in water. (Poggiale.)

¶ *Cyanide of Mercury with Bromide of Calcium.* CaBr,2HgCy + 5Aq. —Dissolves readily in water and alcohol. (Custer.) ¶

Cyanide of Mercury with Chloride of Calcium. CaCl,2HgCy.—Formed by mixing and evaporating the solutions of 7 pts. chloride of calcium and 30 pts. cyanide of mercury. The crystals resemble those of the corresponding strontium-salt. The solution is precipitated by oxalate of ammonia. The crystals are not deliquescent; they dissolve in water and alcohol. (Brett.) The needle-formed crystals contain 6 At. water, effloresce, and dissolve very easily in water. (Poggiale.)

					Brett.
CaCl	55·4	....	18·02	.....	17·0
2 HgCy	252·0	....	81·98	.....	81·1
CaCl,2HgCy	307·4	....	100·00	.....	98·1

Cyanide of Mercury with Chloride of Magnesium. MgCl,2HgCy.—Formed by evaporating a solution of 1 pt. chloride of magnesium and 4 pts. cyanide of mercury. Flat, four-sided prisms, not deliquescent, easily soluble in water, and in weak alcohol. (Poggiale.)

					Brett.
MgCl	47·4	....	15·83	.....	15
2 HgCy	252·0	....	84·17	.....	81
MgCl,2HgCy	299·4	....	100·00	.....	96

Chromidcyanide of potassium forms with mercurous salts a white precipitate, which gradually darkens—the supernatant liquid at the same time at first assuming a brown colour, and then becoming colourless—and is ultimately reduced to a mixture of sesquicyanide of chromium with a small quantity of mercury. With corrosive sublimate no precipitate is formed. (*Berzelius, Lehrb.*)

Cyanide of Mercury with Chromate of Potash. $KO,CrO^3 + 2HgCy$.—The aqueous solution of equal parts of cyanide of silver and monochromate of potash yields, on evaporation, yellow laminated needles, which are permanent in the air, anhydrous, and have a harsh, mercurial taste. These crystals, when heated in a tube, take fire, give off carbonic acid, carbonic oxide, cyanogen and nitrogen gas, together with vapour of mercury, and leave a black, spongy mixture of charcoal, chromic oxide, and cyanate of potash, which, by ignition in the air, is converted into chromate of potash. The salt when treated with strong mineral acids [probably hydrochloric acid ?], gives off hydrocyanic acid. Its aqueous solution is not precipitated by ammonia, potash, or soda, but yields precipitates with soluble metallic sulphides and iodides, and by the salts of baryta, strontia, lime, lead, and iron. The salt dissolves more readily in hot than in cold water. (Caillot & Podevin, *J. Pharm.* 11, 246; also *Kastn. Arch.* 5, 440.)

	Crystallized.			Rammelsberg.
KO	47·2	....	13·44	..... 17·28
CrO^3	52·0	....	14·81	..... 17·60
2 Hg	200·0	....	56·94	..... 51·14
2 Cy	52·0	....	14·81	
$KO,CrO^3,2HgCy$	351·2	....	100·00	

Rammelsberg (*Pogg.* 42, 131), in accordance with his own analysis, assigns to the salt the improbable formula $2(KO,CrO^3) + 3HgCy$; but according to Poggiale (*Compt. rend.* 23, 766,) the true formula is $KO,CrO^3 + 2HgCy$, as above given.

Cyanide of Mercury with Chloride of Manganese. $MnCl,2HgCy$.—Crystallizes with 3 At. water, in transparent, colourless, four-sided prisms, which become rose-coloured by efflorescence, and are very soluble in water. (Poggiale.)

Cyanide of Mercury and Zinc. $ZnCy,HgCy$?—Cyanide of mercury and potassium forms a white precipitate with zinc-salts. (Rammelsberg.)

Cyanide of Mercury with Chloride of Zinc. $ZnCl,2HgCy$.—Forms, with 6 At. water, right four-sided prisms, which are efflorescent and soluble in water. (Poggiale.)

Cyanide of cadmium and potassium produces no turbidity in solution of corrosive sublimate, but throws down metallic mercury from mercurous nitrate. (Rammelsberg.)

Cyanide of Mercury and Lead. $PbCy,HgCy$?—Cyanide of mercury and potassium forms a white precipitate with lead-salts. (Rammelsberg.)

Cyanide of mercury and potassium forms, with ferrous salts, a yellowish brown precipitate, which turns green on exposure to the air. (Rammelsberg.)

Ferrocyanide of potassium, added to mercurous nitrate, throws down a grey mixture of mercury and protocyanide of iron. (Ittner.) The precipitate is white, gelatinous, and assumes a greyish black colour when treated with ammonia. (Wittstein.) It appears in thick, gelatinous, yellowish white flakes, which do not contain any perceptible quantity of separated mercury. (Gm.)

Corrosive sublimate forms, with ferrocyanide of potassium, a white precipitate, which, according to Berzelius, gives up cyanide of mercury to boiling water, leaving a residue of proto-cyanide of iron, and is likewise decomposed, with formation of prussian blue, by mere exposure to the air. According to Ittner, this precipitate is nothing but protocyanide of iron, whilst the liquid retains in solution chloride of potassium and ferruginous cyanide of mercury. Mercuric nitrate also yields a white precipitate with ferrocyanide of potassium. (Wittstein.)

Ferridcyanide of potassium forms, with mercurous nitrate, a thick yellow precipitate (Gm.); a yellowish brown precipitate, which after a while becomes white, and finally green. (Smee.) With mercuric nitrate, ferridcyanide of potassium forms a yellow precipitate (Wittstein); none with corrosive sublimate. (Gm.)

Ammonio-ferrocyanide of Mercury. Hg^2FeCy^3,NH^3,HO.—Obtained by dissolving nitrate of mercuric oxide and ammonia (VI, 95 *c.*) in an ice-cold and moderately strong solution of nitrate of ammonia, containing excess of ammonia, and precipitating the solution with ferrocyanide of

potassium. If the solution of nitrate of ammonia be too concentrated, or warm, mercury is reduced; if it be too dilute, the water exerts a decomposing action; the right degree of concentration must therefore be ascertained by trial, and the precipitation performed in a vessel surrounded with ice. A pale reddish yellow turbidity first appears, but afterwards there are formed wine-yellow, transparent, shining crystals, which seem to be rhombic prisms. The liquid is separated by decantation, and the crystals washed with cold strong ammonia. The crystals give off a portion of their ammonia, even while drying, and after being kept some time, acquire a bluish tinge. Heated in a test-tube, they give off mercury and hydrocyanate of ammonia; when heated in the air, they burn away with emission of sparks and leave ferric oxide. When immersed in water, they turn red, being resolved into cyanide of mercury, ammonia, and ferric oxide, which obstinately retains a small quantity of cyanide of mercury. Aqueous acids separate prussian blue from it, but oil of vitriol heated with it forms a yellow salt, the sulphate of cyanide of mercury, which can only be obtained by this process. (Bunsen, *Pogg.* 31, 139.)

			Bunsen.
NH^3	17	5·12	5·19
Fe	28	8·44	8·58
2 Hg	200	60·24	59·09
3 Cy	78	23·50	
HO	9	2·70	
NH^4O,Hg^2FeCy^3	332	100·00	

Cyanide of Mercury with Ferrocyanide of Potassium. K^2FeCy^3, $3HgCy+4Aq$.—1. Obtained by leaving a hot solution of 1 pt. ferrocyanide of potassium and 2 pts. cyanide of mercury, to crystallize by cooling. (Kane, *Phil. Mag. J.* 16, 128; also *Ann. Pharm.* 35, 356; also *J. pr. Chem.* 19, 405).—2. In preparing cyanide of mercury from ferrocyanide of potassium and mercuric sulphate (p. 13), if the quantity of the latter salt used be too small, the cyanide of mercury produced is mixed with crystals of the compound now under consideration. (Kane.)—3. On boiling ferrocyanide of potassium with mercuric oxide, and filtering to separate the precipitated ferric oxide, pale yellow rhombic crystals are obtained [probably consisting of the same salt]. (Preuss, *Ann. Pharm.* 29, 324.)

Rhombic tables, of a somewhat paler yellow colour than ferrocyanide of potassium. (Kane.)—The salt, when heated, gives up its water and turns white, then fuses, gives off cyanogen and mercury, and moreover yields the decomposition-products of ferrocyanide of potassium. The solution throws down prussian blue from ferrous [ferric] salts. When freed from mercury by sulphuretted hydrogen, it leaves on evaporation pure ferrocyanide of potassium. (Kane.)

The salt obtained by (3) yields when heated, vapour of mercury and the decomposition-products of ferrocyanide of potassium. It dissolves readily in water. If the mercury be removed from the solution by sulphuretted hydrogen, the solution yields on evaporation yellowish tables, which, when treated with acids, effervesce and give off sulphuretted hydrogen. With iodide of potassium the solution forms crystals of the compound of cyanide of mercury with that salt (p. 19); with ferrous salts, a light blue; with ferric salts, a dark blue precipitate; with mercuric nitrate, white translucent flakes; with corrosive sublimate, a white preci-

pitate, which soon turns yellowish; with protochloride of tin, it forms a pasty mixture, with evolution of hydrocyanic acid. (Preuss.)

	Crystallized.		Kane.
2 K	78·4	13·10	12·91
Fe	28·0	4·68	4·47
3 Hg	300·0	50·13	50·13
6 Cy	156·0	26·07	26·71
4 HO	36·0	6·02	5·78
$K^2FeCy^3,3HgCy+4Aq$	598·4	100·00	100·00

Mercurous Cobaltidcyanide?—Cobaltidcyanide of potassium forms a thick white precipitate with mercurous nitrate. (Gm.)

It does not precipitate corrosive sublimate.

Cyanide of Mercury with Chloride of Cobalt. 2CoCl,HgCy.—Crystallizes, with 4 At. water, in yellowish red nodules, which become rose-coloured on exposure to the air, and when heated give off water, cyanogen, and mercury. Their solution is blue when concentrated, rose-coloured when dilute. (Poggiale.)

Aqueous cyanide of nickel and potassium forms, with mercurous nitrate, a bright yellow precipitate, which is immediately converted into a black mixture of cyanide of nickel and metallic mercury, while cyanide of mercury dissolves in the liquid. (Wöhler.)

Cyanide of Mercury with Chloride of Nickel. NiCl,HgCy.—Yields with difficulty greenish blue crystals, containing 6 At. water, and deliquescing in the air. (Poggiale.)

Cuprocyanide of Potassium B (p. 6) added to solution of corrosive sublimate, throws down white flakes. (Gm.)

Cyanide of Mercury with Formiate of Ammonia. $NH^3,C^2H^2O^4+HgCy$.—Triangular prisms which decompose at 200°, yielding water, hydrocyanic acid, and cyanide of mercury. (Poggiale, *Compt. rend.* 23, 766.)

Cyanide of Mercury with Formiate of Potash.—The crystals obtained by Winckler, and already described (p. 282).

Cyanide of Silver. AgCy.—Obtained in the form of a white, curdy precipitate by mixing nitrate or sulphate of silver with hydrocyanic acid or an alkaline hydrocyanate. An excess of the latter redissolves the precipitate. (Scheele, *Opusc.* 2, 165.) It is obtained in the state of greatest purity by precipitating nitrate of silver with cyanide of silver and potassium. If the precipitation be made with cyanide of potassium containing cyanate or carbonate of potash, the precipitated cyanide of silver will also contain cyanate or carbonate of silver, which may be removed by digestion in nitric acid; but if the cyanide of potassium used contains chloride or ferrocyanide of potassium, nitric acid will not remove the impurities thereby introduced. (Glassford & Napier, *Phil. Mag. J.* 25, 66.)—Cyanide of silver is likewise formed by pouring an aqueous solution of nitrate of silver upon cyanide of zinc, cyanide of nickel, prussian blue (in which case heat is required, and its application causes the evolution of nitrous gas), or cyanide of lead (in which case heat must be avoided, because it would cause a separation of metallic silver); the supernatant liquid then contains nitrate of zinc, nickel, iron, or lead. (Wöhler, *Pogg.* 1, 235.)—The cyanide of silver, after washing, must be

dried at a temperature below 126°, because at that temperature it assumes a brownish tint. (Glassford & Napier.)

After drying it forms a white powder.

Cyanide of silver turns brown when exposed to light. (Glassford & Napier.)—When heated out of contact of air, it fuses, gives off half its cyanogen (either as such, or, according to Thaulow, as carbazotic gas) with violent effervescence and a glow extending through the whole mass, and leaves a dull, porous, silver-white globule of paracyanide of silver. $Ag^6C^6N^3$.—Cyanide of silver fuses, with evolution of half its cyanogen, into a mass which is red-brown while hot, but grey when cold, and can only be converted into pure silver by fusion in contact with the air.—It fuses at first with evolution of cyanogen; but afterwards the fusing mass exhibits an appearance of luminosity, and violent effervescence takes place. (Liebig, *Ann. Pharm.* 38, 21.)—It melts quietly at first, then gives off cyanogen, and leaves dicyanide of silver, which at a stronger heat is decomposed, with evolution of light and heat and escape of nitrogen gas (or, according to *Ann. Pharm.* 50, 357, of a combustible gas), and leaves a dull white, fused carbide of silver (VI, 146, 2), which, when treated with dilute nitric acid, leaves a network of charcoal. (Liebig & Redtenbacher, *Ann. Pharm.* 38, 129.)—When fused in an open capsule, or in the bulb of a glass tube, it first turns brown, then black; becomes affected with a boiling motion, gives off gas with violence; exhibits a glow commencing from the sides of the vessel, and rapidly extending throughout the mass; and leaves a button of silver having a dull aspect, or an ash-grey mass of paracyanide of silver. The gas which escapes appears brown from particles of paracyanide of silver mechanically carried forward; as this gas has the same composition per cent. as cyanogen, but somewhat different properties, it is distinguished by the name of *carbazotic gas*. Whilst 134 pts. (1 At.) cyanide of silver give off 14·4 pts. (somewhat more than ½ At.) of cyanogen in the form of carbazotic gas, there remain 11·9 pts. (not quite ½ At.) of cyanogen in the form of paracyanogen, united with the whole of the silver. Hence this silver-residue, when ignited with oxide of copper, yields 2 vol. carbonic acid gas to 1 vol. nitrogen; and when it is treated with dilute nitric acid, the paracyanogen remains undissolved in the form of a black-brown mass. (Vid. *Paracyanogen* and *Paracyanide of Silver*.) (Thaulow.)

The gas evolved in the ignition of cyanide of silver, viz., carbazotic gas, exhibits the following characters: At −4°, it condenses to a transparent and colourless liquid. The gas is colourless; has a density of 1·73; excites tears; irritates the respiratory organs; produces nausea and paleness when inhaled; and has an odour totally different from that of cyanogen.—It burns with a red flame, and is not decomposed by passing through a red-hot tube. Dilute potash-ley absorbs it, acquiring thereby a yellow colour, and separating a substance like paracyanogen. The solution mixed with iron-salts does not yield prussian blue. [The process here employed for forming prussian blue could not well yield it]. Potassium and sodium heated in the gas, burn and are converted into carbazotides; the aqueous solution of these compounds undergoes rapid decomposition; it does not form prussian blue with ferrous salts. [Why was not a ferroso-ferric salt added, and afterwards hydrochloric acid?].—One volume of water at 15° absorbs 4 vol. of the gas. The resulting solution, which reddens litmus, soons deposits paracyanogen, and at the same time emits an odour of cyanogen. (Thaulow, *J. pr. Chem.* 31, 220.)

Liebig (*Ann. Pharm.* 50, 356) finds that, on the one hand, the residue

which remains after the ignition of cyanide of silver, yields when decomposed by oxide of copper, 2 vol. carbonic acid gas to 1 vol. nitrogen; and on the other hand, that the gas evolved (Thaulow's carbazotic gas) is in nowise different from cyanogen. Heated potassium burned in it, and was converted into ordinary cyanide of potassium.—[According to my own experiments, the gas evolved from heated cyanide of silver has exactly the odour of cyanogen; on passing it into aqueous potash, adding a ferroso-ferric salt to the solution, and then hydrochloric acid, prussian blue is formed in considerable quantity. GM.]

Chlorine decomposes cyanide of silver in presence of water, yielding chloride of silver and free cyanogen, which is not converted into chloride of cyanogen till all the cyanide of silver is decomposed. (Liebig, *Pogg.* 15, 571.)—Cyanide of silver heated with half its weight of sulphur is converted into sulphocyanide. (O. Henry, *J. Pharm.* 23, 23.)—Strong nitric or sulphuric acid at a boiling heat decomposes cyanide of silver, and likewise the cyanogen which is set free. (Ittner.) A mixture of equal parts of oil of vitriol and water boiled with cyanide of silver decomposes it, yielding hydrocyanic acid and sulphate of silver; by this means cyanide of silver may be separated from the chloride. (Glassford & Napier, *Phil. Mag. J.* 25, 66.)—Hydrochloric acid instantly decomposes cyanide of silver, yielding chloride of silver and hydrocyanic acid; sulphuretted hydrogen converts it into sulphide of silver and hydrocyanic acid; and sulphide of potassium into sulphide of silver and cyanide of potassium. (Ittner.)—Aqueous solution of corrosive sublimate and cyanide of silver yield, by mutual decomposition, chloride of silver and cyanide of mercury. (O. Henry & Boutron-Charland, *J. Pharm.* 22, 112.)—Cyanide of silver boiled with aqueous solution of chloride or iodide of potassium, yields cyanide of potassium and chloride or iodide of silver. (Liebig, *Schw.* 49, 253.) Similarly with chloride of sodium. (O. Henry.)—Cyanide of silver dissolves in boiling chloride of potassium, sodium, barium, calcium, or magnesium; at ordinary temperatures, however, the solution takes place but slowly. (Glassford & Napier.) [Forming probably a mixture of cyanide of potassium, &c., with a compound of chloride of potassium, &c., and cyanide of silver.]—With aqueous hyposulphite of soda, cyanide of silver forms a solution which yields crystals on evaporation. It likewise dissolves in aqueous ferrocyanide of potassium, forming with it one or two crystallizable salts, which have not been further examined.—It dissolves in aqueous ammonia, and is precipitated therefrom by acids. According to Wittstein, it likewise dissolves in carbonate, sulphate, nitrate, and succinate of ammonia, and in a large excess of hot aqueous sal-ammoniac.—It dissolves sparingly in boiling dilute nitric acid, and separates in a gelatinous form on cooling; but the acid, even when cold and very dilute, dissolves a small quantity of it. (Thaulow, *J. pr. Chem.* 31, 223 and 240.)—Other dilute oxygen-acids, and likewise caustic soda or carbonate of soda, neither decompose nor dissolve it. (Ittner.)

Cyanide of silver unites with other metallic cyanides in equal numbers of atoms, forming compounds called ARGENTOCYANIDES, among which those which are formed by the alkaline cyanides are colourless and soluble in water. (Scheele & Ittner.)

Argentoprussic Acid. HCy,AgCy?—Obtained by precipitating the baryta from argentocyanide of barium with sulphuric acid, and evaporating the filtrate.—Yellowish, slightly acid; smells of hydrocyanic acid,

but is tolerably permanent; combines readily with caustic alkalis; slowly with alkaline carbonates. (Meillet, *N. J. Pharm.* 3, 443.)

Ammonio-cyanide of Silver?—When a dilute solution of nitrate of silver is poured into a hot mixture of ammonia and hydrocyanic acid, and the mixture left to cool quietly, large shining tables are formed. These crystals, when exposed to the air, even at ordinary temperatures, give off all their ammonia, and become milk-white. (Liebig & Redtenbacher, *Ann. Pharm.* 38, 129.)

Nitrocyanide of Silver. $AgO,NO^5+2AgCy$.—Formed by dissolving recently precipitated cyanide of silver, by long-continued boiling, in a somewhat concentrated solution of nitrate of silver. As the liquid cools somewhat below the boiling point, long white shining needles are produced, by which the liquid is converted into a nearly solid mass. These crystals must be dried between filtering paper, without being previously washed with water. They do not contain water. When heated, they melt, and immediately afterwards detonate somewhat violently, leaving cyanide of silver. Hydrochloric acid decomposes them by forming chloride of silver; water, by dissolving the nitrate of silver and separating the pulverulent cyanide. (Wöhler, *Pogg.* 1, 234.)

Crystallized.			Or:			Wöhler.
AgO,NO^5	170	38·58	3 Ag	324	73·97	69·74
2 AgCy	268	61·42	NO^6,2Cy	114	26·03	
AgO,NO^5, + AgCy	438	100·00		438	100·00	

When solution of nitrate of silver is poured upon dicyanide of copper, metallic spangles of silver immediately separate out; on the application of heat, complete decomposition takes place, and water added to the filtrate throws down cyanide of silver, a proof that the compound of nitrate of silver with the cyanide had been formed. [Perhaps in this manner:

$$2Cu^2Cy + 5(AgO,NO^5) = AgO,NO^5,2AgCy + 4\,(CuO,NO^5) + 2Ag].$$

Green cuproso-cupric cyanide immersed in silver-solution is converted into a black substance, which, after being washed and dried, deflagrates with a green light when heated. (Wöhler, *Pogg.* 1, 236.)

Argentocyanide of Potassium. KCy,AgCy.—Discovered by Ittner.—Cyanide of silver dissolves readily in aqueous cyanide of potassium. (Ittner.)—Iodide, as well as chloride of silver, dissolves in aqueous cyanide of potassium. and yields on evaporation crystals which are insoluble in alcohol. (Liebig, *Schw.* 49, 253.) Sulphide of silver does not dissolve in aqueous cyanide of potassium. (Haidlen & Fresenius.) But metallic silver dissolves in the aqueous solution either of cyanide or of ferrocyanide of potassium. (Bagration.)—1 At. chloride of silver dissolves in 2 At. aqueous cyanide of potassium, forming argentocyanide of potassium which crystallizes out first, and chloride of potassium which remains in the mother-liquid. This compound is likewise formed in the decomposition of cyanate of silver, of Ag^2FeCy^3 and $3AgCy,Fe^2Cy^3$, by aqueous cyanide of potassium. (Glassford & Napier.)—The compound is prepared by saturating aqueous cyanide of potassium with cyanide of silver, and evaporating to the crystallizing point. (Ittner.)

Regular octohedrons, often with scalariform depressions in the faces; before purification by recrystallizing, they form plumose, striated laminæ. (Rammelsberg, *Pogg.* 38, 376.) Colourless, six-sided laminæ [probably

octohedral segments] or plumose crystals. (Ittner.) Sometimes six-sided tables, sometimes small, transparent, rhombic prisms, which appear to contain 1 At. water and become turbid in drying. (Glassford & Napier.) Permanent in the air, neutral to vegetable colours; they are inodorous, and have a sweet taste, but leave an unpleasant metallic after-taste. (Ittner.) Permanently bitter, according to Glassford and Napier.

	Crystallized.			Rammelsberg.		Glassford & Napier. *a.*		*b.*
K	39·2	19·68		20·19		19·28		18·59
Ag	108·0	54·22		52·58		53·72		51·48
2 Cy	52·0	26·10				26·00		25·08
KCy,AgCy	199·2	100·00				99·00		98·15

The crystals analyzed by Rammelsberg had been previously dried at 150°, whereby they lost ½ per cent. of water. Glassford & Napier dried their crystals at 105°, because, at higher temperatures, the crystals were found to become brownish and friable. *a* are the six-sided tables, *b* the rhombic prisms, which, on account of the loss observed (independently of the drying at 105°), are likewise supposed to contain 1 At. water.

The solution of the salt exposed to the action of the galvanic current deposits silver at the cathode, whilst, at the anode, if it consists of silver, an equal quantity of that metal is dissolved. (Napier, *Phil. Mag. J.* 25, 379.) The solution must contain excess of cyanide of potassium; otherwise the positive silver plate becomes covered with the cyanide of silver as it forms, and this compound being a bad conductor of electricity, stops the current of weak batteries. If aqueous cyanide of potassium be placed on the positive side, and aqueous argentocyanide of potassium on the negative side, the two being separated by a porous diaphragm, a battery of four pairs is sufficient to produce rapid decomposition. During the first twelve hours, nothing but silver is deposited at the negative pole; but afterwards hydrogen gas begins to escape,—a proof that cyanide of potassium is also decomposed; and the liquid in the negative cell then acquires the odour of hydrocyanic acid, exhibits a strong alkaline reaction, and contains merely cyanide of potassium, with a small quantity of cyanide of silver. It is only when the current is rather strong that cyanide of potassium is decomposed at the beginning of the action as well as cyanide of silver, and consequently, hydrogen evolved. If the positive pole consists of platinum, a feeble current is sufficient to produce decomposition, even when the solution does not contain excess of cyanide of potassium. The cyanogen set free at the positive pole dissolves in the liquid, and produces a dark brown colouring and a blackish precipitate. With a battery of eight pairs, however, oxygen gas is evolved at the positive pole, and cyanide of silver is deposited upon it. (Napier.)

Light blackens the crystals, and likewise a piece of paper moistened with the aqueous solution, but not the solution itself. (Glassford & Napier.)—Hydrosulphuric acid and the alkaline hydrosulphates throw down sulphide of silver from the solution. (Ittner.)—All the stronger acids, in a state of dilution, and even acetic acid, precipitate the cyanide of silver from the solution; and the precipitate may then be converted by hydrochloric acid into chloride of silver and hydrocyanic acid, whereas the oxygen-acids exert no further action upon it. An action, similar to that of the free acids, is likewise produced by the salts of antimonic, stannous, stannic, and ferric oxides, which throw down cyanide of silver

mixed with the oxide contained in the precipitant. (Ittner.) The caustic alkalis and their hydrochlorates exert no action (Ittner); neither do the alkaline carbonates. (Glassford & Napier.)—The salt dissolves in 8 pts. of cold water, in 1 part of boiling water; also in boiling alcohol, from which it crystallizes on cooling. (Glassford and Napier; comp. Gay-Lussac, *Gilb.* 53–59.)

Argentocyanide of Calcium.—The precipitate produced by cyanide of calcium in a solution of nitrate of silver dissolves in excess of the latter, forming a liquid which is not clouded either by sal-ammoniac or by hydrochloric acid. (Scheele.)

Chromidcyanide of Silver. $3AgCy,Cr^2Cy^3$.—Chromidcyanide of potassium forms a white precipitate with silver-salts. The dried precipitate is resolved by heat into cyanogen gas, silver, and cyanide of chromium. By hydrosulphuric acid and water, it is converted into sulphuric acid and hydrochromidcyanic acid. (Böckmann, *Liebig Chim. org.* 1, 174.)

Argentocyanide of Manganese.—$MnCy,AgCy$.—Formed by precipitating a manganous salt with argentocyanide of silver. The greyish white precipitate (bluish white according to Gay-Lussac; white according to Gm.), is decomposed by hydrochloric acid, yielding hydrocyanic acid, chloride of manganese, and a precipitate of cyanide of silver. (Ittner.)—According to Glassford and Napier, manganous sulphate is not precipitated by argentocyanide of potassium.

Manganidcyanide of Silver. $3AgCy,Mn^2Cy^3$.—Manganidcyanide of potassium yields, with nitrate of silver, a yellowish brown precipitate, which, if the silver-salt is in excess, and a certain quantity of free acid is present, assumes, after a while, a scarlet colour, but recovers its brown hue when washed. (Rammelsberg, *Pogg.* 42, 117.)

Argentocyanide of Zinc.—Argentocyanide of potassium forms a white precipitate with zinc-salts. (Ittner, Glassford & Napier.)

Argentocyanide of Cadmium.—Cyanide of cadmium and potassium forms, with nitrate of silver, a white precipitate, which dissolves in excess of the cyanide of cadmium and potassium, and from which nitric acid throws down cyanide of silver. (Rammelsberg.)

Argentocyanide of Lead.—Argentocyanide of potassium forms a white precipitate with lead-salts. (Ittner.)

Argentocyanide of Iron.—Ferrous salts form, with argentocyanide of potassium, a greenish precipitate (white, according to Gay-Lussac; brownish white, according to Glassf. & Nap.; brownish yellow-white, according to Gm.), which is resolved by hydrochloric acid into protocyanide of iron, chloride of silver, and hydrocyanic acid, and is insoluble in acids. (Ittner.) It is capable of combining with ammonia. (Monthiers, *N. J. Pharm.* 11, 253.)

Ferrocyanide of Silver. $C^6N^3FeAg^2 = Ag^2FeCy^3$.—The white precipitate which ferrocyanide of potassium forms with silver-salts. It acquires a bluish tint by exposure to the air (Ittner), or when dried at too high a temperature. When heated, it first gives off the cyanogen belonging to the silver, then the nitrogen of the cyanide of iron, and is converted, with emission of a glowing light, into a mixture of silver (which may be extracted by mercury), and bicarbide of iron (Berzelius,

Schw. 30, 51).—It dissolves, with some decomposition, in oil of vitriol, leaving a yellowish residue; the colourless solution, when exposed to the air, deposits crystalline grains of sulphate of silver. (Berzelius, *Schw.* 30, 51.)—Nitric acid immediately decomposes this white compound, extracting $\frac{1}{4}$ of its silver, and converting it into the orange-yellow compound $3AgCy,Fe^2Cy^3$. (Glassford & Napier.) Other acids, even hydrochloric acid, exert no decomposing action. (Ittner.) Aqueous potash forms ferrocyanide of potassium and separates oxide of silver. (Ittner.) Aqueous cyanide of potassium dissolves the compound, forming argentocyanide and ferrocyanide of potassium. (Glassford & Napier, *Phil. Mag. J.* 25, 71):

$$Ag^2FeCy^3 + 4KCy = 2(KCy,AgCy) + K^2FeCy^3.$$

The precipitate dissolves in ammonia, forming an opalescent liquid, but is insoluble in ammoniacal salts. (Wittstein.)

Ferridcyanide of Silver. $C^6N^3Ag^3,C^6N^3Fe^2=3AgCy,Fe^2Cy^3$.—Ferridcyanide of potassium forms, with nitrate of silver, a thick, orange-yellow precipitate. (Gm.) This precipitate, heated under water to about 66°, turns green, and afterwards retains that colour. If the precipitate retains a small quantity of acid or of nitrate of silver, it does not turn green till heated in the dry state.—When treated with a comparatively small quantity of aqueous cyanide of potassium, it is converted into ferridcyanide of potassium and cyanide of silver; with a large quantity, into ferridcyanide and argentocyanide of potassium. (Glassford & Napier.)

$$3AgCy,Fe^2Cy^3 + 3KCy = 3KCy,Fe^2Cy^3 + 3AgCy;$$

and:

$$3AgCy,Fe^2Cy^3 + 6KCy = 3KCy,Fe^2Cy^3 + 3(KCy,AgCy).$$

The precipitate dissolves quickly in ammonia, forming a yellow solution; also in hot carbonate of ammonia, the solution becoming turbid as it cools; but not in other ammoniacal salts. (Wittstein.)

Argentocyanide of Cobalt? CoCy,AgCy?—The pale red precipitate which cobalt-salts form with argentocyanide of potassium. (Glassford & Napier.)

Cobaltidcyanide of Silver. $C^6N^3Ag^3C^6N^3Co^2=3AgCy,Co^2Cy^3$? — Cobaltidcyanide of potassium forms a white precipitate with silver-salts. (Gm.) ¶ The precipitate is white, curdy, insoluble in water and in acids; it is anhydrous, and not altered by exposure to light. (Zwenger, *Ann. Pharm.* 62, 177.)

				Zwenger.
2 Co	59	71·05		70·74
3 Ag	324			
12 C	72	13·35		13·56
6 N	84	15·60		
$Ag^3Co^2Cy^6$	539	100·00		

Ammonio-cobaltidcyanide of Silver. $NH^3,HO,Ag^3Co^2Cy^6$.—Cobaltidcyanide of silver dissolves in ammonia, forming a solution, which, when evaporated, yields the ammonio-cobaltidcyanide in colourless transparent prisms. These crystals are insoluble in water, and do not lose weight, either by exposure to the air, or by a heat of 100°. At 170°, water and ammonia (together amounting to 4·97 pts.) go off, and cobaltidcyanide of silver remains undecomposed. Acids readily withdraw the ammonia. (Zwenger.)

				Zwenger.	
2 Co	59	67·75	67·62	67·15	
3 Ag	324				
7 N	98	17·37			
12 C	72	12·75	12·57		
4 H	4	0·71	1·11	0·81	
1 O	8	1·42			
$NH^3,HO,Ag^3Co^2Cy^6$	565	100·00 ¶.			

Argentocyanide of Nickel. NiCy,AgCy?—Cyanide of nickel and potassium, added to a solution of silver, throws down white flocks, which remain white when exposed to light, and dissolve in ammonia, but not in nitric acid. (F. & E. Rodgers.)

Cuprocyanide of Silver.—a. AgCy,Cu^2Cy?—Cuprocyanide of potassium A yields, with nitrate of silver, a white precipitate, which becomes bluish grey when treated with a larger quantity of silver-solution, and yellowish white when treated with nitric acid, a small quantity of cyanogen being at the same time evolved. (Rammelsberg.)

b. 3AgCy,Cu^2Cy?—Cuprocyanide of potassium B forms, with solution of silver, white, curdy flakes, which soon turn violet and afterwards black (Gm.), and dissolve in an excess of the potassium-salt B. (Rammelsberg.)

Argentocyanide of Copper. CuCy,AgCy?—Argentocyanide of potassium forms, with cupric salts, a bluish white precipitate (light green, according to Glassford & Napier), from which acids extract the copper, and separate cyanide of silver. (Ittner.)

Argentocyanide of Mercury. HgCy,AgCy?—Argentocyanide of potassium forms a white precipitate with corrosive sublimate (Glassford & Napier); so likewise does cyanide of mercury and potassium with silver-salts. (Rammelsberg.)

Cyanide of Mercury with Nitrate of Silver. AgO,NO^5,2HgCy.—On mixing the aqueous solutions of nitrate of silver and cyanide of mercury, this compound separates, after a while, in transparent and colourless prisms, which are small if the solutions are cold, and large, like those of nitre, if they are hot. (Wöhler, *Pogg.* 1, 231.)

	Crystallized.		Wöhler.	Johnston.
AgO,NO^5	170	37·12	37·96	37·53
2 HgCy	252	55·02	53·74	54·54
4 Aq	36	7·86	7·60	7·93
AgO,NO^5 + 2HgCy + 4Aq. .	458	100·00	99·30	100·00

The crystals give off 7·6 per cent. of water, even below 100°, and are converted into a white, opaque mass, which, when heated above 100°, melts to a transparent liquid, then boils, and immediately afterwards detonates violently with a crackling noise, and the purple-red flame which is characteristic of cyanogen; cyanide of silver remains behind, and a sublimate of mercury is found to have been formed.—Hydrochloric acid eliminates hydrocyanic acid; then, on evaporation, chlorine is given off, and chloride of silver remains behind (32·2 per cent.), together with chloride of mercury. The aqueous solution, mixed with chloride of barium, yields a precipitate of chloride of silver, while [illegible] of mercury and nitrate of baryta remain in solution.—Hydro-

cyanic acid, added to the solution, throws down all the silver in the form of cyanide; and the supernatant liquid, when evaporated, gives off the nitric acid, and leaves 53·74 per cent. of cyanide of mercury.—Alkalis throw down cyanide of silver.—The crystals dissolve very sparingly in cold water, but much more readily in boiling water, from which they separate again on cooling. They are soluble without decomposition in boiling nitric acid, and dissolve in alcohol in about the same proportion as in water. (Wöhler, *comp.* Johnston, *Phil. Trans.* 1839, 117.)

In a solution of cyanide of silver in nitrate of mercury, no precipitate is formed by nitric acid or nitrate of silver; but hydrocyanic acid added to such a solution, throws down cyanide of silver, and hydrochloric acid or a metallic chloride throws down chloride of silver. (Wackenroder, *Ann. Pharm.* 41, 317.)

PROTOCYANIDE OF GOLD, or AUROUS CYANIDE. AuCy.—*Formation.*—Cyanide of calcium forms a white [?] precipitate with solution of chloride of gold (Scheele); cyanide of potassium forms an orange-yellow precipitate. (Ittner.) The precipitate is yellow, crystalline, dissolves in excess of cyanide of potassium, reappears on addition of a small quantity of hydrochloric acid, and disappears on the addition of a larger quantity. (Haidlen & Fresenius.) The concentrated normal solution of chloride of gold (VI. 216), even when in excess, is not precipitated by cyanide of potassium, but merely decolorized, because auro-cyanide of potassium is formed, which crystallizes on evaporation. (Rammelsberg.)—Figuier's statement that the normal solution of chloride of gold also forms the yellow precipitate with cyanide of potassium, is likewise contradicted by Himly.—That, in this case, terchloride of gold, yields, not tercyanide but protocyanide of gold, is due to the evolution of 2 At. cyanogen.—The solution of chloride of gold does not become turbid when mixed with aqueous cyanide of mercury; but, on the addition of alcohol, the mixture forms a precipitate resembling cyanide of palladium. (G. Rose, *Pogg.* 23, 173.)—This mixture, when evaporated, gives off cyanogen gas, and leaves a mixture of aurous cyanide and chloride of mercury. (Defferre.)—Aqueous aurocyanide of potassium, mixed with hydrochloric or nitric acid, does not yield a precipitate of aurous cyanide till the mixture is heated. (Himly, Carty, Glassford & Napier.)—Corrosive sublimate, added to aurocyanide of potassium, immediately throws down the yellow compound. (Rammelsberg, *Pogg.* 42, 132.)

Preparation. 1. The cyanide of gold is precipitated from the aqueous solution of aurocyanide of potassium, by heating that solution with hydrochloric or nitric acid. The mixture of aqueous aurocyanide of potassium and hydrochloric acid, which is transparent at ordinary temperatures, is heated to 50°, whereby the greater part of the aurous cyanide is precipitated in the form of a lemon-yellow crystalline powder; the mixture evaporated to dryness over the water-bath, in order to produce complete decomposition, whereupon the hydrocyanic acid of the cyanide of potassium is given off; and the residue, which consists of cyanide of gold and chloride of potassium, is washed with water, in a situation not exposed to sunshine, in order to remove the chloride of potassium. (R. Himly, *Ann. Pharm.* 42, 157.)—The solution of aurocyanide of potassium in a small quantity of water is heated to the boiling point in hydrochloric or nitric acid, the mixture evaporated to dryness, and the residue thoroughly washed with ice-cold water.—The concentrated solution of the

chloride of gold may likewise be supersaturated with cyanide of potassium till the aurous cyanide first precipitated is re-dissolved; the mixture evaporated to dryness; the residue heated with hydrochloric or nitric acid, to decompose the cyanide of potassium; the excess of acid expelled by evaporation, and the dry residue washed with cold water. The product thus obtained may, however, be contaminated with silica, if the cyanide of potassium has been prepared in an earthen crucible,—(Glassford & Napier, *Phil. Mag. J.* 25, 61).—J. Carty, (*Phil. Mag.* J. 24, 515) mixes the solution of chloride of gold with a quantity of cyanide of potassium sufficient to redissolve the precipitate; boils the liquid with excess of hydrochloric acid; washes the precipitated yellow powder; and dries it a gentle heat.

2. By precipitating a solution of chloride of gold with cyanide of potassium,—Figuier (*J. Pharm.* 22, 329,) cautiously adds a solution of cyanide of potassium in 6 pts. water to a normal solution of chloride of gold (VI, 216), containing 5 pts. water to 1 pt. chloride of gold, till a copious lemon-yellow precipitate is produced, which then slowly settles down. If a larger quantity of cyanide of potassium be used, the precipitate has a dirty yellow colour, and is more quickly deposited; a still larger quantity renders it orange-yellow, but a small quantity of nitric acid restores the lemon-yellow colour.

3. By mixing the hydrochloric acid solution of gold with cyanide of mercury, evaporating to dryness, and extracting the resulting chloride of mercury from the residue by water:

$$AuCl^3 + 3HgCy = 3HgCl + AuCy + 2Cy.$$

Defferre (*J. Pharm.* 24, 27,) adds to the solution of 2 pts. gold in heated aqua-regia, a solution of 3 pts. cyanide of mercury in 8 pts. water; evaporates, stirring all the while, till the residue turns yellow; digests the residue in 24 pts. of water, which leaves cyanide of gold undissolved; mixes the decanted solution with 1 pt. cyanide of mercury; evaporates again; redissolves in water, which again leaves cyanide of gold; and repeats this solution, decantation, and evaporation from 1 to 3 times, as long as lemon-yellow cyanide of gold continues to separate, not however adding cyanide of mercury at each repetition of the process. A small quantity of aqua-regia must however be added before each evaporation; otherwise brick-red cyanide of gold will be left undissolved.—[Since, according to the preceding equation, 199 pts. (1 At.) gold, require 3 . 126 pts. (3 At.) cyanide of mercury, = 199 : 378, it would perhaps be better to take at once 2 pts. cyanide of mercury to 1 part of dissolved gold.]—This process yields only half as much cyanide of gold as might be expected, the other half forming, in fact, a soluble compound with the cyanide of mercury. The dried residue should therefore be washed, not with water, but with alcohol, which dissolves the chloride of mercury and the excess of cyanide of mercury, but only a trace of cyanide of gold. With this precaution the process gives very good results. (Desfosses.)

4. By heating hydrate of auric oxide with hydrocyanic acid, and evaporating the mixture to dryness;

$$AuO^3 + 3HCy = 3HO + AuCy + 2Cy?.$$

The hydrate prepared with magnesia, according to Pelletier's process, (VI, 208,) assumes, when boiled with the hydrocyanic acid, first a blackish green, and then, on boiling, a fine yellow colour,—and the residue obtained by gentle evaporation does not require washing.

5. On evaporating a solution of tercyanide of gold in boiling hydrochloric acid, a protocyanide of gold is deposited in the form of a yellow powder, 2 At. cyanogen being probably decomposed at the same time. (Carty.)

Properties. Lemon-yellow crystalline powder, iridescent in sunshine, and appearing, under the microscope, to consist of regular six-sided tables. (Himly.) Inodorous, tasteless, and permanent in the air. (Figuier.) Permanent in the air. (Glassford & Napier.)

			Himly.	Carty.	Glassford & Napier.	Iwreinov.	Rammelsberg.	Figuier.
Au....	199	88·44	87·84	87·95	88·18	88·19	76	75
Cy....	26	11·56						
AuCy	225	100·00						

The powder is anhydrous, and therefore merely requires to be freed from hygroscopic water by drying in vacuo. (Himly.)

Decompositions. Protocyanide of gold, when dry, is not altered by exposure to sunshine, but, when moist, it acquires a dingy yellow colour, with a tinge of green. (Himly.) By ignition it is resolved into cyanogen gas and metallic gold. (Figuier, Himly, and others.) According to Proust, it is resolved into water, an empyreumatic oil, carbonic oxide, and a mixture of gold and charcoal. When heated in contact with air, it burns away with a glimmering light, leaving metallic gold. (Rammelsberg.) It is not decomposed or dissolved by sulphuric, hydrochloric, nitric, or nitro-hydrochloric acid, even at a boiling heat. (Figuier, Himly.) When recently precipitated, it is soluble to a slight extent in sulphuric, hydrochloric, or nitric acid. (Glassford & Napier.) It is converted into metallic gold by boiling oil of vitriol, and very slowly decomposed by boiling aqua-regia. (Carty.) Oil of vitriol, caustic alkalis, and alkaline carbonates, colour it green, but the yellow colour is restored on the addition of hydrochloric acid. (Jewreinov, *J. pr. Chem.* 32, 242.) Aurous cyanide is not decomposed by sulphuretted hydrogen; but hydrosulphate of ammonia dissolves it completely after a while, forming a colourless liquid from which acids throw down sulphide of gold. (Himly.) It dissolves in ammonia. (Glassford & Napier.) It is not altered by cold potash-ley; but a strong solution of potash at a boiling heat converts it into brown pulverulent gold and aurocyanide of potassium. [Himly.] [What becomes of the oxygen of the potash; is cyanate of potash likewise formed?]

The compound dissolves in hyposulphite of soda (Glassford & Napier); also in aqueous cyanide of potassium. It is insoluble in water, alcohol, and ether. (Figuier, Himly.)

Protocyanide of gold unites in equal numbers of atoms with other metallic cyanides, forming compounds called *Aurocyanides*, among which those of the alkalis are colourless and soluble in water. Those which contain the cyanides of the heavy metals are obtained by precipitating a salt of the heavy metal with aurocyanide of potassium; they are insoluble in water, and, when treated with an alkali, give up the cyanide of gold together with the cyanide which was united with the other heavy metal, leaving the oxide of that metal undissolved. (Ittner.)

Tercyanide of Gold, or *Auric Cyanide?* $AuCy^3$ [or $HCy,AuCy^3$?] Discovered by K. Himly.—*Preparation.* 1. It may be separated from auridcyanide of potassium by the addition of one of the stronger acids.—

2. More conveniently: An aqueous solution of auridcyanide of potassium is mixed with excess of nitrate of silver; the liquid, containing the excess of the silver-salt, together with nitrate of potash, is filtered; the precipitate, consisting of AgCy, $AuCy^3$, thoroughly washed with water; then diffused in water, and decomposed with frequent agitation, and at the ordinary, or at a very slightly elevated temperature (otherwise a yellow colouring will appear, and protocyanide of gold will be formed), by a quantity of hydrochloric acid, not sufficient to decompose the whole; and the filtrate evaporated to dryness in vacuo over oil of vitriol and lime. — 3. Auridcyanide of potassium is mixed with hydrofluosilicic acid and evaporated to dryness; the residue exhausted with absolute alcohol; and the solution filtered from the silico-fluoride of potassium, and left to evaporate. (Himly.) The tercyanide of gold thus obtained generally has a yellowish colour, arising from the admixture of a small quantity of protocyanide; it must therefore be dissolved in the smallest possible quantity of water or alcohol, and the filtrate left to evaporate in the air or in vacuo; for the application of heat would reproduce cyanide of gold. (Himly.)

Large colourless laminæ and tables, containing 6 At. water of crystallization. (Himly.)

They fuse at 50°, first giving off hydrocyanic acid, yielding a lower cyanide of gold, then cyanogen gas, and leave carbide of gold, which readily burns in the air, and is converted into pure gold. The aqueous solution, when evaporated over the water-bath, deposits part of the gold in the form of protocyanide. A boiling aqueous solution of oxalic acid exerts no reducing action. Mercurous or mercuric nitrate, heated with the solution, throws down protocyanide of gold, while cyanide of mercury remains in solution. Corrosive sublimate forms no precipitate even when the solution is heated. Tercyanide of gold does not become moist when exposed to the air, but dissolves in water in every proportion, and almost as easily in alcohol and ether. (Himly.)

Crystallized.			Himly.	*Second Calculation.*		
Au	199	60·12	59·89	Au	199	60·12
3 Cy	78	23·57		3 Cy	78	23·57
6 Aq	54	16·31		HCy	27	8·16
				3 Aq	27	8·15
$AuCy^3$,6Aq.	331	100·00		HCy,$AuCy^3$+3Aq.	331	100·00

[As Himly only determined the quantity of gold, he has by no means proved that the compound is really $AuCy^3$+6 Aq; it is more probable, indeed, that the real composition is that which is indicated in the preceding table under the head of "Second Calculation." For in the decomposition of AgCy, $AuCy^3$ by HCl, the products formed must be AgCl and HCy, $AuCy^3$ (auriprussic acid), and similarly in the other modes of preparation. It is likewise observed by Himly himself that the compound when heated, gives off at first, not cyanogen but hydrocyanic acid.]

Ammonio-protocyanide of Gold—The solution of protocyanide of gold in hot aqueous ammonia yields, on cooling, a large quantity of the compound in grey shining laminæ, which are easily deprived of their ammonia, either by a gentle heat or by treatment with hydrochloric acid. (Carty).

Aurocyanide of Ammonium. NH^4Cy,AuCy.—Formed by mixing the saturated aqueous solutions of aurocyanide of potassium and sulphate of ammonia; precipitating therefrom the sulphate of potash and excess of

ulphate of ammonia by absolute alcohol; and leaving the filtrate to evaporate to the crystallizing point. Very small, colourless, anhydrous crystals, having a strongly metallic taste. They are resolved, between 200° and 250°, into cyanide of ammonium, which evaporates, and a residue of cyanide of gold, which retains the form of the crystals. (Himly, *Ann. Pharm.* 42, 342.)

	Crystallized.		Himly.
NH^4Cy	44	16·36	16·10
Au	199	73·97	73·64
Cy	26	9·67	10·26
$NH^4Cy,AuCy$	269	100·00	100·00

Auridcyanide of Ammonium. $NH^4Cy,AuCy^3$.—Hydrated auric oxide is added to hydrocyanate of ammonia, obtained by distilling ferrocyanide of potassium with sal-ammoniac and water, as long as it continues to dissolve; the colourless filtrate is heated, which causes a large quantity of ammonia to escape; the filtrate evaporated over the water-bath, during which process it becomes covered with a rusty yellow film; the dry residue exhausted with water; and the filtrate left to evaporate till it crystallizes.—Large, colourless, four- and six-sided tables. At 100° they give off 5·06 per cent. of water and turn reddish-white; at a higher temperature, they turn yellow and give off hydrocyanate of ammonia; and when ignited in the air leave 58·7 per cent. of pure gold. They dissolve readily in water and alcohol, but are nearly insoluble in ether. (Himly, *Ann. Pharm.* 42, 343.)

	Crystallized.		Himly.
NH^4Cy	44	12·98	
Au	199	58·70	58·71
3 Cy	78	23·01	
2 HO	18	5·31	5·06
$NH^4Cy,AuCy^3+2Aq$	339	100·00	

The rusty yellow substance (*vid. sup.*), which separates on evaporating the solution, detonates slightly when heated; is insoluble in water, acids, alkalis, alcohol, or ether; and consists perhaps of aurate of ammonia (VI, 222). Himly.

Aurocyanide of Potassium. KCy,AuCy.—The easiest mode of forming this compound is to dissolve protocyanide of gold in aqueous cyanide of potassium. But, according to Prince Peter Bagration (*J. pr. Chem.* 31, 367), gold precipitated by green vitriol likewise dissolves in that liquid, especially with the aid of heat; even a plate of gold will dissolve in it, especially if exposed to the joint action of the solution of cyanide of potassium and of the air. Ferrocyanide of potassium likewise dissolves gold, though in much smaller quantity, even after continued digestion. [In this case, as shown by Elsner (*J. pr. Chem.* 37, 333), access of air is necessary, and potash is formed at the same time:

$$2KCy + Au + O = KCy,AuCy + KO.$$

As the cyanide of potassium used by Bagration contained cyanate of potash, the oxygen was perhaps partly supplied by this latter compound]. —Auric oxide, both anhydrous and hydrated, and aurate of ammonia, likewise dissolve completely in aqueous cyanide of potassium, and form this compound. According to Himly, the solution of the hydrated oxide

is attended with evolution of heat. In this reaction, Himly supposes that cyanate of potash is formed as well as free potash, as shown by the following equation:

$$AuO^3 + 3KCy = KCy,AuCy + KCyO^2 + KO.$$

Hence, according to Himly, this solution of hydrated auric oxide when evaporated gives off ammonia, proceeding from the decomposition of cyanate of potash.

Preparation. 1. Aqueous cyanide of potassium is saturated by agitation with protocyanide of gold, and the yellow [?] filtrate evaporated to the crystallizing point. (Ittner.)—77 pts. of cyanide of gold require 23 pts. of cyanide of potassium dissolved in water. (Himly.)

2. For every 1 pt. of gold to be dissolved, 6 pts. of cyanide of potassium are dissolved in from twice to four times their quantity of water. In the filtrate heated to 38°, are immersed two plates of gold, the smaller of which is connected by a copper wire with the negative pole of a three-pair battery of zinc and copper, and the other, which is several times larger, with the positive pole. Of the gold which dissolves quickly at the positive pole, only a small quantity is at first deposited in brown crystalline granules on the negative gold plate, where at the same time a slight disengagement of gas takes place. After a few hours, the cyanide of potassium is found to be saturated with cyanide of gold; and when that point is attained, the quantity of gold deposited at the negative pole is equal to that which is dissolved in the same time at the positive pole. In this manner half an ounce of gold yields, in a few hours, 1 oz. of crystals of aurocyanide of potassium. (Glassford & Napier, *Phil. Mag. J.* 25, 61.)

3. By dissolving auric oxide (prepared by precipitating chloride of gold with magnesia, dissolving the precipitate in strong nitric acid, and filtering through muslin into water, which precipitates the oxide) in aqueous cyanide of potassium. (Glassford & Napier.)

4. By dissolving fulminating gold in aqueous cyanide of potassium, whereupon ammonia is evolved. (Himly.)—The fulminating gold precipitated by excess of ammonia from a solution of 7 pts. of gold in aqua-regia, and well washed, is added to a hot aqueous solution of 6 pts. of pure cyanide of potassium. The colourless solution, if not too dilute, yields crystals as it cools: the mother-liquid, on further evaporation, yields merely an impure salt, containing much potash; hence it is best to evaporate, after mixing it with excess of hydrochloric acid, and free the remaining aurous cyanide from chloride of potassium by digestion in water. The cyanide of gold thus obtained may be converted into aurocyanide of potassium by the first method (23 pts. cyanide of potassium to 77 pts. cyanide of gold).—The resulting crystals are purified by dissolving them in an equal quantity of boiling water and crystallizing. Crystallization takes place very quickly as the liquid cools; in 10 minutes, prisms an inch long are formed. (Himly, *Ann. Pharm.* 42, 160.)

Properties. Large, colourless (yellow, according to Ittner only), transparent crystals. Rhombic octohedrons united endwise into long prisms, like those of sulphur. (Himly.)—White nacreous scales. (Meillet.)—Has a saline sweetish taste, with a somewhat metallic after-taste (Himly); metallic (Ittner); bitter and metallic (Glassford & Napier).—Permanent in the air (Himly), even in sunshine (Jewreinov, *J. pr. Chem.*

32, 242). The solution does not redden the fingers when moistened with it, even on exposure to light. (Glassford & Napier.)

	Crystallized.			Himly.	Jewreinov.	Glassford & Napier.
K	39·2	13·51		14·04	13·54	
Au	199·0	68·57		68·46	67·96	66·54
2 Cy	52·0	17·92			18·47	
KCy,AuCy	290·2	100·00			99·97	

The crystals do not undergo any change at 100°; when heated to 130°, they give off only 0·39 per cent. of water, which is therefore nothing but adhering moisture, and nothing further at 200°. (Himly.) According to Jewreinov, they do not give off any water when heated.—Glassford & Napier, on the contrary, calculate, from the quantity of gold obtained, that the crystals contain 1 At. water.

Decompositions. The salt, when heated out of contact with the air, is resolved into cyanogen gas, and a mixture of gold and cyanide of potassium. (Carty, *Phil. Mag. J.* 24, 515.) Complete decomposition takes place only at a very strong red heat. (Himly.) The salt, when ignited, decrepitates; fuses, with effervescence and evolution of cyanogen; and covers the platinum crucible with gold, which, after the residue has been heated with water, amounts to only 11·44 per cent, while the solution still retains gold. (Jewreinov, *J. pr. Chem.* 32, 242.) [This solution must also contain platinum.] When the salt is very strongly ignited with an equal weight of carbonate of potash, a button of gold is obtained, amounting to 66·54 per cent. (Glassford & Napier.) Iodine added to the solution throws down cyanide of gold, with formation of iodide of potassium and liberation of cyanogen (Gerdy, *Compt. rend.* 16, 25; also *J. pr. Chem.* 29, 181);

$$KCy,AuCy + I = AuCy + KI + Cy.$$

Heated with oil of vitriol, it gives off hydrocyanic acid, and after strong ignition leaves a mixture of gold and sulphate of potash. (Jewreinov.) Its solution, mixed with hydrochloric, sulphuric, or nitric acid, at ordinary temperatures, remains clear at first, but afterwards gives off hydrocyanic acid, and gradually deposits part of the gold in the form of protocyanide. (Glassford & Napier, Carty, Jewreinov.) But when boiled down with hydrochloric acid, it is completely resolved into cyanide of gold, amounting to 87·83 per cent, according to Himly, and to 88·5 p. c. according to Glassford & Napier, and chloride of potassium. Similar reactions are produced by sulphuric and nitric acid, and even by oxalic, tartaric, and acetic acid at a boiling heat. (Glassford & Napier.) The salts of bismuth-oxide, zinc-oxide, lead-oxide, and ferric-oxide throw down from the solution a mixture of cyanide of gold and one of these oxides. (Ittner.) The aqueous solution, mixed with aqueous corrosive sublimate, yields, without evolution of hydrocyanic acid, a pale yellow precipitate, which increases at a boiling heat, and gradually assumes the dark yellow colour of aurous cyanide; the solution contains cyanide of mercury and chloride of potassium, and is perfectly free from gold. (Ittner, Himly.)

$$KCy,AuCy + HgCl = KCl + HgCl + AuCy.$$

Alkaline hydrosulphates produce no change in the solution. (Ittner.) The aqueous solution gilds copper and silver, especially when heated,

and even without the aid of the electric current, the copper and silver ultimately dissolving in it. (Bagration.)

The salt dissolves in 7 pts. of cold water, in ½ pt. boiling water (Himly); in 4 pts. cold and 0·8 pt. boiling water. (Glassford & Napier.) From a solution saturated in the cold, it is precipitated undecomposed by sulphuric, hydrochloric, or nitric acid; alcohol added to the aqueous solution, saturated while warm, gradually throws down the salt in white, opaque, highly lustrous scales. (Glassford & Napier.) It dissolves very sparingly in alcohol, the solubility being somewhat greater at a boiling heat; the dryer the alcohol, the less of the salt does it dissolve. (Himly.) Insoluble in ether. (Himly.)

The solution is particularly well adapted for galvanic gilding (I, 497). To obtain the remaining gold from such gilding solutions, after they have become inactive, they should be evaporated to dryness; the residue finely pulverized and intimately mixed with an equal quantity of litharge; fused at a strong red heat; and the lead extracted from the button of lead and gold by warm nitric acid; the gold then remains in the form of a loose, yellowish brown, spongy mass (Böttger, *J. pr. Chem.* 36, 169; confirmed by Elsner, Redtel, Hessenberg, *J. pr. Chem.* 37, 447; 38, 169 and 256).

Auridcyanide of Potassium. $KCy,AuCy^3$.—Formed by converting 7 pts. of gold into a solution of the chloride as neutral as possible, and gradually adding this liquid to a hot concentrated aqueous solution of 8 pts. cyanide of potassium. The colourless mixture, as it cools, deposits crystals, which may be purified by recrystallization:

$$AuCl^3 + 4KCy = KCy,AuCy^3 + 3KCl.$$

(Himly, *Ann. Pharm.* 42, 340.) A similar process is adopted by Rammelsberg (*Pogg.* 42, 133).

Large, colourless tables (Himly). Meillet (*N. J. Pharm.* 3, 443), on evaporating a mixture of the two solutions, obtained white, pearly scales.

When exposed to the air, they effloresce quickly and turn milk-white; in vacuo (Himly) or at 100° (Rammelsberg) they give off all their water of crystallization. The residue then melts to a brown liquid, from which part of the gold separates out, an evolution of cyanogen taking place at the same time. (Rammelsberg.) The salt, when heated, gives off 2 At. cyanogen, and is converted into KCy,AuCy. (Himly.)—Chlorine exerts a decomposing action only when aided by heat, chloride of cyanogen being then formed. (Rammelsberg.) Acids added to the solution of the salt produce no precipitate, but colour it yellow and eliminate hydrocyanic acid. (Rammelsberg.) Corrosive sublimate throws down yellow cyanide of gold (Rammelsberg); it forms no precipitate, because the $AuCy^3$ produced is soluble in water. (Himly.) [?] Mercurous nitrate boiled with the solution forms a yellowish precipitate. (Himly.) The salt does not dissolve in absolute alcohol. (Himly.) Its aqueous solution is the best of all materials for galvanic gilding. (Meillet.)

	Dried above 100°.		Rammelsberg.	Himly.
K	39·2	11·46	11·43	11·47
Au	199·0	58·15	57·54	57·18
4 Cy	104·0	30·39		
$KCy,AuCy^3$	342·2	100·00		

The crystals contain, according to Rammelsberg, 3·39, according to Himly, 3·76 per cent. of water. [2 At. water would amount to 5 per cent.]

While Rammelsberg and Himly, by supersaturating chloride of gold with cyanide of potassium, obtained the salt $KCy,AuCy^3$, Glassford & Napier, on the contrary, found that this process yields the salt KCy,AuCy, and they make the following statements respecting the reaction: The first portions of the concentrated solutions of cyanide of potassium (prepared by Rodgers's process, and containing cyanate of potash), which are added to the cold concentrated solution of chloride of gold, and serve to saturate the excess of hydrochloric acid and the nitric acid, excite strong effervescence, arising from the escape of carbonic acid, ammonia, and hydrocyanic acid. The subsequent portions of cyanide of potassium then decompose the solution of chloride of gold, as represented by the following equation:

$$AuCl^3 + 4KCy + 4HO = KCy,AuCy + 3KCl + HCy + 2CO^2 + NH^3.$$

[If this equation be correct, carbonic acid must be given off during the whole reaction.] —But if the solution of chloride of gold be hot, aurate of ammonia is at first precipitated together with the cyanide of gold; and on further addition of cyanide of potassium, this aurate of ammonia is redissolved with evolution of ammonia.

Cyanide of Gold and Calcium.—The precipitate formed by hydrocyanate of lime in a solution of chloride of gold, dissolves in excess of the hydrocyanate of lime, producing a colourless liquid. (Scheele.)

Aurocyanides of Manganese, Zinc, Tin, Lead, and Iron.—The aqueous solution of aurocyanide of potassium forms small crystals with protochloride of manganese. (Glassford & Napier.) With sulphate of zinc it forms a white precipitate. (Glassford & Napier.) With protochloride or bichloride of tin, it forms a yellowish white precipitate, which is decomposed by hydrochloric acid into hydrocyanic acid, chloride of tin, and a residue of gold. (Ittner.) With sugar of lead, a white precipitate. (Glassford & Napier.) With green vitriol, a green precipitate, according to Ittner, but, according to Glassford & Napier, a white precipitate which is coloured purple by nitric acid.

Cyanide of Copper and Gold?—Cuprocyanide of potassium A precipitates terchloride of gold, and aurocyanide of potassium precipitates cupric salts yellowish green; acids extract the copper from both precipitates, and leave yellow cyanide of gold. (Ittner.)—Aurocyanide of potassium forms a white precipitate with nitrate of copper. (Glassford & Napier.)

With nitrate of mercury, aurocyanide of potassium forms a yellowish white precipitate. (Glassford & Napier.)

Aurocyanide of Silver. AgCy,AuCy.—Aurocyanide of potassium forms, with nitrate of silver, a white curdy precipitate, which appears to be the compound AgCy,AuCy, and not a mere mixture, inasmuch as it does not exhibit any trace of yellow colour. When treated with ammonia, it leaves a white substance, which, when exposed to light, quickly assumes a dark colour. (Himly.)

Auridcyanide of Silver. $AgCy,AuCy^3$.—Formed by precipitating nitrate of silver with auridcyanide of potassium. The curdy precipitate

darkens on exposure to light, and dissolves in ammonia, but not in nitric acid. (Himly.) The yellowish white precipitate which Glassford & Napier obtained by precipitating terchloride of gold with argentocyanide of potassium, is perhaps a mixture of this compound with chloride of silver:

$$AuCl^3 + 2(KCy,AgCy) = AgCy,AuCy^3 + AgCl + 2KCl.$$

PROTOCYANIDE OF PLATINUM, or PLATINOUS CYANIDE. PtCy.—Gm. (*Handb.* Aufl. 2, 2, 1692) discovered *Platinocyanide of potassium;* Döbereiner (*Pogg.* 37, 546; also *Ann. Pharm.* 17, 250) prepared from that compound, *Protocyanide of platinum*, and *Platinoprussic acid;* Knop (*Ann. Pharm*, 43, 111) discovered the salt which he called *Platinidcyanide of potassium;* and Knop & Schnedermann (*J. pr. Chem.* 37, 461) pointed out the methods of preparing several other salts belonging to the same class.—¶ Quadrat (*Ann. Pharm.* 63, 164; 70, 309) has discovered a class of platinocyanides having the general formula $Pt^5M^6Cy^{11}$ or $5(PtMCy^2) + MCy$. If $PtCy^2$ be regarded as a compound radical, *Platino-cyanogen*, which may be denoted by the symbol Cpty, the formula of Quadrat's salts, may also be written: 5MCpty + MCy. The existence of these salts cannot, however, be regarded as positively established. They may, after all, be nothing but platinocyanides contaminated with some impurity which Quadrat did not succeed in separating. At all events, Laurent and Gerhardt, in analysing the potassium-salt prepared by Quadrat's method, have obtained results agreeing exactly with Gmelin's platinocyanide of potassium (*vid.* p. 47). The whole matter therefore requires further examination. ¶

Preparation of Platinous Cyanide.—1. The precipitate PtCy,HgCy, which platinocyanide of potassium forms with mercurous nitrate, is freed from mercurous nitrate by boiling with water, whereby it loses its blue colour; it is then dried, and heated to redness in a small glass retort. (Döbereiner, *Pogg.* 37, 546; also *Ann. Pharm.* 17, 250.) If access of air be prevented, the heat may be raised to low redness. (Knop & Schnedermann.)—2. Platinocyanide of potassium dried over oil of vitriol is heated in a retort with corrosive sublimate till no further reaction is apparent; and the residue is freed by hot water from chloride of potassium, then dried and sublimed, to free it from calomel. (Knop & Schnedermann.) Probably thus:

$$KCy,PtCy + 2HgCl = KCl + Hg^2Cl + PtCy + Cy.$$

3. Platinocyanide of potassium, after being well dried in oil of vitriol, is dissolved in that liquid, and a small quantity of water added; strong heat is thereby produced, and protocyanide of platinum separates out. If too much water be added, the rise of temperature is not sufficient to cause the separation of the platinous cyanide. To remove the cyanide of potassium which adheres to this precipitate, it is ignited with sal-ammoniac, whereupon cyanide of ammonium is evolved, and then freed from chloride of potassium by digestion in water. (Knop & Schnedermann.)

Prepared by (1), it is greenish yellow (Döbereiner, Rammelsberg); by (2), yellowish green; by (3), sulphur-yellow, in the fresh stage; but when dry, it exhibits a dark, rusty brown colour, and conchoidal fracture; appears red-brown in small fragments by transmitted light; but when pulverized, again yields a sulphur-yellow powder.

When heated in the air, it burns away, and leaves from 78 to 79 per cent of platinum. (Döbereiner.) That which is prepared by (3) leaves only 76 per cent. of platinum, because it contains a certain quantity of chloride of potassium. (Knop & Schnedermann.)—It is insoluble in water, acids, and alkalis. (Döbereiner.) The preparation (3), when recently precipitated, and not having been ignited with sal-ammoniac, dissolves in

ammonia and in hydrocyanate of ammonia; the preparation (2) does not. (Knop and Schnedermann.)

Protocyanide of platinum combines with other metallic cyanides.

Pt	99	....	79·20
Cy	26	....	20·80
PtCy	125	....	100·00

¶ Quadrat found in the cyanide prepared by Döbereiner's method only 71·68 p. c. of platinum, and in that prepared by Knop & Schnedermann's process (3), only 72·84 p. c. He is of opinion that the protocyanide of platinum has never yet been obtained in the pure state. The numbers which he obtained correspond much more nearly with the formula Pt^2Cy^3, which requires 71·54 per cent. of platinum. (*Ann. Pharm.* 65, 186). ¶

Hydroplatinocyanic Acid. HCy,PtCy?—Obtained by suspending in water the above-mentioned precipitate, produced from platinocyanide of potassium and nitrate of mercury; passing sulphuretted hydrogen through the liquid; filtering from sulphide of mercury; and leaving the filtrate to crystallize by slow evaporation.—¶ Quadrat uses, instead of the mercury-salt above-mentioned, the copper-salt, $Pt^5Cu^6Cy^{11}$. In decomposing this salt by sulphuretted hydrogen, the presence of ammonia must be carefully avoided, because the separated acid rapidly takes up any of that base that may be present, forming with it an ammonia-salt which can scarcely be distinguished from the acid. The liquid filtered from the sulphide of copper (which being very finely divided, does not settle down till it has been heated, and left to stand for a day) is evaporated to dryness, and exhausted with a mixture of alcohol and ether, from which the acid crystallizes on evaporation. The decomposition of the copper-salt is likewise attended with the production of hydrocyanic acid. Thus:

$$Pt^5Cu^6Cy^{11} + 6HS = 6CuS + HCy + 5PtHCy^2.$$

(*Ann. Pharm.* 63, 198.) ¶

Hydroplatinocyanic acid crystallizes in needles, united in stellate groups, and exhibiting either a golden or a copper-coloured metallic lustre. By rapid evaporation, a greenish yellow substance is obtained, which likewise exhibits two metallic colours on the surface. When the solution in absolute alcohol is abandoned to spontaneous evaporation, crystals are produced exhibiting beautiful chameleon tints. (Döbereiner.) —¶ According to Quadrat, the acid crystallizes by slow evaporation, in bluish black prisms, containing water of crystallization; by rapid crystallization, in fine greenish yellow crystals, exhibiting sometimes a golden, sometimes a coppery lustre. ¶—The acid reddens litmus strongly. It does not decompose by exposure to light, or to a temperature of 100°; but, above 100°, it is resolved into hydrocyanic acid and monocyanide of platinum. ¶ At 100°, it turns yellow, reddish yellow, and ultimately white: it is not decomposed at 140°. (Quadrat.) ¶ When its alcoholic solution, mixed with a little nitric acid, is evaporated on a glass surface, and the residue strongly heated, a very beautiful platinum mirror is produced. (Döbereiner.)

The acid deliquesces in moist air, dissolves very readily in water and alcohol, and unites with the alkalis forming Platinocyanides. (Döbereiner.) —¶ The carbonates are decomposed by it, carbonic acid escaping, water being formed, and a platinocyanide of the metal produced. It is an extremely delicate reagent for ammonia, which it absorbs, forming an ammoniacal salt, and acquiring a yellow colour. Sulphuric acid decom-

poses it with the aid of heat, a yellow substance, protocyanide of platinum, being separated, and hydrocyanic acid escaping. (Quadrat.)

				Quadrat.
Pt	99	65·07		65·04
H	1	0·63		0·62
2 Cy	52	34·30		34·14
HCy,PtCy	152	100·00		99·80 ¶.

Bicyanide of Platinum, or *Platinic Cyanide*, is not known in the separate state, but occurs in combination with the cyanides and chlorides of other metals.

Ammonio-protocyanide of Platinum, $NH^3,PtCy$; *Cyanide of Platosammonium*, NH^3Pt,Cy; or *Hydrocyanate of Platosamine*, NH^2Pt,HCy.—1. The solution of $2NH^3,PtO$ (VI, 296 C, *a*) mixed with hydrochloric acid yields a precipitate of NH^3PtCy, hydrocyanate of ammonia NH^3,HCy being formed at the same time (Reiset, *Compt. rend.* 18, 1102):

$$2NH^3,PtO + 2HCy = NH^3PtCy + NH^4Cy + HO.$$

¶ 2. When chloride of platosammonium (VI, 302, *b*) is digested with excess of cyanide of silver, the decanted liquid yields, on concentration, fine regular needles of a pale yellow colour, soluble with tolerable facility in water and ammonia; their analysis shows them to have the composition of cyanide of platosammonium. (Buckton, *Chem. Soc. Qu. J.* 4, 34.)

			Buckton.
NH^3	17	11·97	
Pt	99	69·72	69·35
Cy	26	18·31	
NH^3Pt,Cy	142	100·00	

Platinocyanide of Diplatosammonium. $N^2H^6Pt,PtCy^2 = N^2H^6PtCy,PtCy$.—Isomeric with the compound last described: $2(NH^3Pt,Cy = N^2H^6Pt,PtCy^2$.—1. Cyanogen gas passed into a moderately concentrated solution of diplatosamine (VI, 296, C, *a*) is slowly absorbed; and, after a while, this compound separates out in the form of a yellowish white, crystalline substance, its formation going on till the colour of the solution changes, from partial decomposition of the cyanogen: the mother-liquor contains carbonate of ammonia and carbonate of diplatosamine. The reaction depends upon the decomposition of water, the elements of which uniting with the cyanogen, form hydrocyanic and cyanic acids. The hydrocyanic acid forms platinocyanide of diplatosammonium, ammonia, and water:

$$2(N^2H^6PtO,HO) + 2HCy = N^2H^6Pt,PtCy^2 + 2NH^3 + 4HO;$$

and the cyanic acid forms at first cyanate of diplatosamine, which, by taking up the elements of water, is immediately resolved into carbonate of diplatosamine and carbonate of ammonia:

$$N^2H^6PtO,CyO + 4HO = N^2H^6PtO,CO^2 + NH^4O,CO^2.$$

The crystals of the platinocyanide are easily purified by recrystallization from water.—2. By mixing a solution of hydrochlorate of diplatosamine (VI, 300, N, *a*) with cyanide of potassium, a precipitate is formed consisting of this compound, which may be purified by several recrystallizations. This method yields the compound more easily and in greater

quantity than the former.—3. By saturating oxide of diplatosammonium with hydroplatinocyanic acid, or mixing hydrochlorate of diplatosamine with platinocyanide of potassium.

This compound, when purified by recrystallization, forms crystals, which, under the microscope, appear like six-sided tables, arranged in stellate groups. It is soluble without decomposition in potash, hydrochloric acid, and dilute sulphuric acid; strong sulphuric and nitric acid decompose it. Its aqueous solution forms, with nitrate of silver, a white precipitate of platinocyanide of silver, while nitrate of diplatosamine remains in solution:

$$N^2H^6Pt,PtCy^2 + AgO,NO^5 = N^2H^6PtO,NO^5 + AgPtCy^2?$$

	Calculation.		Buckton.
4 C	24	8·45	
6 H	6	2·11	
4 N	56	19·72	20·16
2 Pt	198	69·72	69·48
$N^2H^6Pt,PtCy^2$	284	100·00	

(Buckton, *Chem. Soc. Qu. J.* 4, 26.) ¶

Platinocyanide of Ammonium $NH^4Cy,PtCy$.—Obtained by dissolving protocyanide of platinum prepared by (3), and recently precipitated (not previously ignited with sal-ammoniac) in aqueous hydrocyanate of ammonia, and evaporating to the crystallizing point. Since cyanide of platinum (prepared by 3) always contains more or less cyanide of potassium, the crystals formed by this process are somewhat contaminated with platinocyanide of potassium.

Long colourless needles, with conspicuous steel-blue glitter. When exposed to the air, they immediately give off water, and acquire an orange-yellow colour. When placed over oil of vitriol at ordinary temperatures, they give up all their water, excepting 1 per cent., which escapes between 100° and 120°. (Knop & Schnedermann.)

¶ When dry ammoniacal gas is passed over hydroplatinocyanic acid previously dried at 100°, care being taken to keep the acid in excess, the latter assumes a yellow colour; an excess of ammonia destroys this colour, and makes the compound white again. The white compound, when exposed to the air, turns yellow, from loss of ammonia, and then exhibits an acid reaction.

On mixing the aqueous solutions of platinocyanide of potassium and sulphate of ammonia, evaporating to dryness, and exhausting with alcohol, the solution yields, on cooling, prismatic crystals, which are colourless while they remain in the liquid, but on exposure to the air, turn yellow, give off ammonia, and become acid; on being introduced into an atmosphere of ammonia, they again become colourless. (Quadrat.)

Platino-platinidcyanide of Ammonium.—$(NH^4)^6Pt^5Cy^{11} = NH^4Cy, 5(NH^4PtCy^2.)$—Obtained by mixing the solution of the corresponding potassium-salt with sulphate of ammonia, evaporating to dryness, and digesting with alcohol, to separate sulphate of potash and excess of sulphate of ammonia. The alcoholic solution, when evaporated, yields delicate needle-shaped crystals, having a lemon-yellow colour, with a tinge of lavender, violet, or even rose-colour, and a strong diamond lustre. They are very soluble in water, and yield a colourless solution; when dried, they turn brown, but do not alter in composition. (Quadrat.)

			Quadrat.
6 NH^4	108	12·15	11·68
5 Pt	495	55·68	56·21
11 Cy	286	32·17	32·11
$NH^4Cy,5(NH^4PtCy^2)$	889	100·00	100·00

Platinidcyanide of Ammonium. $NH^4Cy,PtCy^2$.—Formed by treating the preceding salt, $NH^4Cy,PtCy$, with chlorine, exactly in the same manner as the salt $KCy,PtCy$ is converted into $KCy,PtCy^3$. The solution yields beautiful needles, having a coppery lustre, with a tinge of greenish brown. (Knop & Schnedermann.) According to these chemists, the formula of the salt is $2NH^4Cy,Pt^2Cy^3 + 5Aq$. (See the corresponding potassium salt.)

Bicyanide of Platinum with Chloride of Ammonium. $NH^4Cl,PtCy^2$.—Formed by dissolving the last-mentioned salt in hot dilute aqua-regia, and evaporating to the crystallizing point.—Isomorphous with the corresponding potassium-salt.—When heated, it gives off sal-ammoniac and cyanogen, and leaves yellow protocyanide of platinum. Aqueous ammonia converts it successively into the compounds $NH^4Cy,PtCy$ and $NH^4Cy,PtCy^2$. (Knop & Schnedermann.) See the corresponding potassium-salt.

Platinocyanide of Potassium. $KCy,PtCy$.—Formed by fusing cyanide or ferrocyanide of potassium with platinum; hence platinum crucibles are strongly attacked by alkaline cyanides in a state of fusion. (Gm.) — 1. A mixture of equal parts of spongy platinum and ferrocyanide of potassium is heated nearly to redness in a glass or crucible (if the heat applied be insufficient, the ferrocyanide of potassium remains undecomposed, and if it be too great, the platinum-salt is decomposed); the mass is dissolved in water; the filtrate evaporated at a gentle heat; the warm liquid separated by decantation from any crystals of undecomposed ferrocyanide of potassium that may have been formed; then left to cool, till the platinum-salt crystallizes; and this salt purified by pressure between paper and recrystallization, both from ferrocyanide and from cyanide of potassium. (Gm.)—2. Bichloride of platinum is converted by heat into protochloride; an aqueous solution of cyanide of potassium completely saturated with the latter; and the filtrate evaporated and left to crystallize (Knop):

$$PtCl + 2KCy = KCy,PtCy + KCl.$$

Since a large quantity of platinum-salt remains dissolved in the mother-liquor which contains the chloride of potassium, it must be evaporated and mixed with oil of vitriol; hydrochloric acid is then evolved, and a yellow gummy precipitate formed, consisting of protocyanide of platinum, which separates almost completely on boiling the liquid with excess of sulphuric acid. The liquid is then diluted with water, and the precipitate thrown on a filter; washed with water; dissolved hot in aqueous cyanide of potassium; the liquid boiled till the evolution of ammonia (from the cyanate of potash) ceases; and then brought to the crystallizing point. (Knop and Schnedermann.)—3. A concentrated solution of bichloride of platinum is added to the aqueous solution of cyanide of potassium, the mixture heated till the precipitate, consisting of chloroplatinate and chloroplatinite of potassium, is redissolved, and then left to crystallize. The liquid effervesces when heated, giving off a large quantity of carbonate of ammonia, proceeding from cyanate of potash contained in the cyanide of potassium. (Meillet,

N. J. Pharm. 3, 444.)—As $PtCl^2$ was used in this preparation, cyanogen and other products of decomposition must have been likewise evolved. (Gm.)

$$PtCl^2 + 3KCy = KCy,PtCy + 2KCl + Cy.$$

¶ 4. When the salt $K^6Pt^5Cy^{11}$ is boiled continuously with water and the solution repeatedly crystallized, compounds are obtained successively richer in platinum, till at length the maximum 51·98 p. c. is obtained. (Quadrat, *Ann. Pharm.* 70, 301.) ¶

Long needles and thicker rhombic prisms. *Fig.* 64. without the *i*- and *i i*- faces. $\acute{u} : u = 97°$; $a : u = 122°$.—Pale yellow by transmitted light, and by reflected light falling obliquely on the axis of the prisms; bright blue by reflected light falling more in the direction of the axis. (Gm.)

Dried at 200°.		Rammelsberg.	Quadrat.	*Crystallized.*		Gm.
K.....	39·2	20·61	21·00	K....	39·2	18·05	17·74
Pt.....	99·0	52·05	50·49	51·98	Pt..	99·0	45·58	45·22
2 Cy	52·0	27·34		2 Cy .	52·0	23·94	
				3 Aq .	27·0	12·43	12·40
$KPtCy^2$.	190·2	100·00		+3Aq....	217·2	100·00	

The crystals effloresce rapidly in the air, becoming opaque and rose-coloured; at 100°, they give off 12·4 per cent. of water, assuming first a white and then an orange-yellow colour. At a higher temperature, the residue gives off 0·22 p. c. more water (12·62 p. c. in all) again becoming white, and ultimately fusing into a grey and yellow mass, which is very apt to run over the sides of the vessel. (Gm.) The dry salt heated out of contact with the air does not decompose at any temperature between 400° and 600°. (Knop & Schnedermann.)—Nitric acid decomposes the salt, forming nitre and a transparent and colourless jelly. Mixed with an equal weight of oil of vitriol and with water, and evaporated, it forms a yellow, tenacious mass. Dilute sulphuric acid colours it orange-yellow. (Gm.)—It dissolves in oil of vitriol without evolution of hydrocyanic acid; the solution heated to the boiling point yields protocyanide of platinum in thick yellow flakes, no hydrocyanic acid escaping, but a gas which burns with a blue flame, probably carbonic oxide. If the quantity of water added to the sulphuric acid solution be just sufficient to produce intense heat, the cyanide of platinum still separates out; but if too much water be added, it does not. (Knop & Schnedermann.)—The salt dissolves abundantly in warm water, but a considerable portion separates out very quickly as the liquid cools. (Gm.)

¶ *Platino-platinidcyanide of Potassium.* $K^6Pt^5Cy^{11} = KCy,5KPtCy^2$.—1. Obtained by adding protochloride of platinum (prepared by evaporating a solution of platinum in aqua-regia and heating the residue to the melting point of tin) to an excess of a recently prepared solution of cyanide of potassium. The resulting colourless solution filtered and evaporated to the crystallizing point yields, after a while, beautiful yellow crystals, which, if the crystallization has been rapid, are almost chemically pure. If the platinous chloride is in excess, the salt does not crystallize so readily. In both cases, hydrocyanic acid escapes during the evaporation. By one recrystallization the crystals may be obtained quite pure; and if the solution be left to evaporate slowly in the air, crystals may be obtained 2 or 3 inches long, and from half a line to a line in thickness. — 2. The salt may likewise be prepared by mixing bichloride of platinum with

cyanide of potassium; in this case, however, it is contaminated with chloroplatinate of potassium.—3. By decomposing the impure salt obtained by (2), with strong sulphuric acid, adding water, boiling as long as protocyanide of platinum continues to separate out in the form of a yellow gelatinous body, washing this substance with water, dissolving in cyanide of potassium, and evaporating to the crystallizing point, a nearly pure salt may be obtained; but the first method yields the purest product.

This salt, when crystallized by slow evaporation, forms long, thin, prismatic crystals, yellow by transmitted, blue by reflected light. It dissolves very readily in hot water, crystallizing out as the solution cools; in alcohol and ether it is less soluble. When exposed to the air, especially in summer, it effloresces readily and turns white; and if the exposure be long continued, it assumes a pale rose-colour, an effect which takes place, even if the salt has been previously dried at 100°. When heated, it first turns white, then yellow, and afterwards fuses and is decomposed. Boiling oil of vitriol separates protocyanide of platinum from it; not pure, however, but contaminated with sulphate of potash, which cannot be removed by washing with water. With mercurous and mercuric salts it forms white precipitates; but on adding an excess of a mercurous salt (the nitrate) a copious smalt-blue precipitate is found. This affords an extremely delicate test for the cyanogen-compounds of platinum.—One part of the salt dissolves in 3 pts. of water at 16°. In boiling water it is much more soluble, and crystallizes out on cooling. It dissolves also, though less readily, in alcohol and in ether.

The crystals contain 15·98 p. c. (21 At.) water, of which 14·03 p. c. (18 At.) go off at 100°. (Quadrat, *Ann. Pharm.* 63, 167.)

Anhydrous.			Quadrat (*mean*).
6 K	235·2	23·13	23·19
5 Pt	495·0	48·72	48·38
11 Cy	286·0	28·15	27·69
$KCy,5PtKCy^2$	1016·2	100·00	

Crystallized.			Quadrat.
6 K	235·2	19·50	
5 Pt	495·0	41·08	
11 Cy	286·0	23·74	
21 Aq	189·0	15·68	15·98
+21Aq	1205·2	100·00	

Gerhardt (*Laur. & Gerh. C. R.* 1850, 146) has analyzed the salt prepared by Quadrat's method, and found it to contain: 17·8 p.c. potassium, 45·0 platinum, 24·9 cyanogen, and 12·3 water, numbers corresponding as nearly as possible with Gmelin's formula of the platinocyanide of potassium (p. 47). A like result has been obtained by Laurent (*Compt. rend.* 1848, tom. 26). If the analyses made by Laurent and Gerhardt are correct, and were really performed on the same salt as that obtained by Quadrat, it must follow that all the corresponding salts prepared by Quadrat, the so-called platinoplatinidcyanides, are nothing more than platinocyanides. The question, must, however, for the present be regard as undecided. ¶

Platinidcyanide of Potassium. KCy,PtCy ?—According to Knop, it is a Sesquicyanide of Platinum and Potassium $=2KCy,Pt^2Cy^3$.—When chlorine gas is passed into a saturated solution of platinocyanide of potassium, fine copper-coloured needles are soon deposited. As soon as the liquid coagulates from this cause into a solid mass, the stream of chlorine must be interrupted, otherwise the crystals will be decomposed. The needles

must be left to drain in a funnel; pressed strongly between paper; dissolved in the smallest possible quantity of hot water, to which a small quantity of hydrochloric acid has been added to decompose the carbonate and cyanate of potash which adhere to them, and would reduce the salt to the platinocyanide; and the solution left to crystallize by cooling. The salt cannot be washed either with water or with alcohol; for the former would dissolve too much of it, and the latter would precipitate the mother-liquid. (Knop.)—If the platinocyanide of potassium used in the process is but very slightly contaminated with carbonate of potash, the chlorine may still be passed through its cold saturated solution; but a larger quantity of carbonate forms hypochlorite of potash, which exerts a decomposing action on the platinum-salt. Instead of chlorine, bromine may be used, or if great care be taken, aqua-regia. (Knop & Schnedermann.) The equation for the formation of this salt, is probably the following:

$$3KPtCy^2 + 2Cl = 2KPtCy^3 + KPtCl^2.$$

Slender copper-coloured needles matted together; under the microscope they appear as flat four-sided prisms, which have a pale green colour by transmitted light, as may be seen in sunshine with the naked eye.

Crystallized.	Calculation according to Gm.				Calculation according to Knop.		Knop.
K	39·2	....	16·12	2 K	78·4	.... 17·37	.... 17·55
Pt	99·0	....	40·71	2 Pt	198·0	.... 43·86	.... 43·45
6 C	36·0	....	14·80	10 C	60·0	.... 13·29	.... 14·33
3 N	42·0	....	17·27	5 N	70·0	.... 15·51	
3 Aq	27·0	....	11·10	5 Aq	45·0	.... 9·97	.... 10·36
$KCy,PtCy^2+3Aq$	243·2	....	100·00	$2KCy,Pt^2Cy^3+5Aq$	451·4	....	100·00

	Calculation, according to Gerhardt.			Gerhardt.
2 K	78·4	....	17·03	..... 17·0
2 Pt	198·0	....	43·02	
5 Cy	130·0	....	28·23	..... 28·2
6 Aq	54·0	....	11·72	..... 11·7
$2KCy,Pt^2Cy^3+6Aq$	460·4	....	100·00	

The quantities of potassium, platinum, and water found by Knop agree best with his own formula, but that of the platinum is more favourable to mine; the latter also is recommended by its greater simplicity, as well as by the circumstance that compounds of 2 At. platinum with 3 At. of a salt-radical do not generally occur. ¶ Gerhardt (*N. J. Pharm.* 10, 223) considering the existence of a sesquicyanide of platinum as improbable, suspected some error in Knop's analysis, and gave the preference to Gmelin's formula. Subsequently however (*Laur. & Gerh. C. R.* 1850, 145) he has found, by the analysis of a very pure specimen, that Knop's formula is correct, excepting that it contains 1 At. water too little (*vid. sup.*) Nevertheless he regards the salt, not as containing a sesquicyanide of platinum, but as a compound of platinidcyanide of potassium with protocyanide of platinum $=2KCy,PtCy^2+PtCy+6Aq$. ¶

The salt, when placed in vacuo over oil of vitriol, gives off its water of crystallization even at ordinary temperatures, at the same time turning black and becoming partially insoluble in water. When heated, it first turns black and gives off cyanogen; but afterwards becomes yellowish white, and ultimately fuses to a brown mass. When ignited with three times its weight of sal-ammoniac, it leaves platinum and chloride of potassium free from cyanide. It is decomposed by hot oil of vitriol, with separation of a yellowish powder, which gives off cyanogen at a red heat, and leaves a residue containing platinum and potassium. When treated

with cold concentrated hydrochloric acid, it first turns orange-yellow, then becomes colourless, but resumes its copper colour when heated. By digestion with aqueous carbonate of potash, this salt is reconverted into platinocyanide of potassium. (Knop.)

$$2(KCy,PtCy^2) + 2KO = 2(KCy,PtCy) + KCy + KCyO^2. \text{ (Gm.)}$$

Ammonia added in proper proportion likewise effects this reduction. (Knop.) The salt dissolves very readily and without colour in water; but the solution when evaporated and cooled again, yields the red needles. (Knop.)

Bicyanide of Platinum with Chloride of Potassium. $KCl,PtCy^2$.—Obtained by dissolving the preceding salt in dilute aqua-regia at a nearly boiling heat, evaporating the solution over the water-bath to the crystallizing point, mechanically separating the large crystals thus obtained from the admixed crystals of chloride of potassium, and purifying them by repeated crystallization. (Knop & Schnedermann.) [In the formation of these crystals, cyanogen must either be set free or be decomposed by the aqua-regia: $KPtCy^2 + Cl = KCl,PtCy^2 + Cy$.—Whence comes the KCl?]

Very large, colourless crystals belonging to the oblique prismatic system. *Fig.* 121, either truncated at the edges between u and v (with the face n), between v and u behind (with the face w), and between v and the lower y (with the face x);—or truncated on the edge between u and v with the face n, sufficiently to obliterate the face u, and likewise at the summit between y, v, and the hinder u (with the face z).—$y : u = 112° 30'$; $y : v = 102° 45'$; $u : v = 103°$; $u : n = 144° 30'$; $v : n = 137°$; $v : w = 123°$; $y : z = 134°$. (Naumann, *J. pr. Chem.* 37, 465.)—The crystals effloresce very rapidly, and give off all their water of crystallization, amounting to 7·86 p. c. (2 At.), even at a gentle heat; at a stronger heat they give off cyanogen; after gentle ignition they leave a mixture of chloride of potassium and protocyanide of platinum; and after strong ignition, a mixture of chloride of potassium and metallic platinum.—The salt, when dissolved in water may, by the action of zinc, or of sulphurous acid gas passed through the solution, or of ammonia, be brought back to the preceding salt, or to the salt KCy,PtCy. (Knop & Schnedermann.)—Reduction to the preceding salts, according to Gm.

a. By zinc:

$$2(KCl,PtCy^2) + Zn = KCy,PtCy^2 + PtCy + KCl + ZnCl;$$

and:

$$KCl,PtCy^2 + Zn = KCy,PtCy + ZnCl.$$

b. By sulphurous acid:

$$2(KCl,PtCy^2) + SO^2 + 2HO = KCy,PtCy^2 + PtCy + KO,SO^2 + 2HCl;$$

and:

$$KCl,PtCy^2 + SO^2 + HO = KCy,PtCy + SO^3 + HCl.$$

According to Knop and Schnedermann, the first equation in the case o sulphurous acid is:

$$3(KCl,PtCy^2) + 2SO^2 + 3HO = 2KCy,Pt^2Cy^3 + PtCy + KO,2SO^3 + 3HCl;$$

the second equation agrees with that above given.

	Dried.		Knop & Schnedermann.
K	39·2	17·38	18·32
Cl	35·4	15·69	15·26
Pt	99·0	43·88	43·15
2 Cy	52·0	23·05	
$KCl,PtCy^2$	225·6	100·00	

¶ *Platinocyanide of Sodium.* NaCy,PtCy.—Formed by boiling an excess of the copper-salt CuCy,PtCy with carbonate of soda, then filtering and evaporating.—Large colourless, transparent crystals belonging to the oblique prismatic (monoclinometric) system, soluble in water and alcohol. The solution often forms a bright red precipitate with mercurous nitrate. (Quadrat, *Ann. Pharm.* 79, 303.)

			Quadrat.
Na	23·2	13·23	13·10
Pt	99·0	56·75	56·53
2 Cy	52·0	30·02	
NaCy,PtCy	174·0	100·00	

Platinoplatinidcyanide of Sodium. $Na^6Pt^5Cy^{11}$=NaCy,5NaPtCy^2.—Obtained by boiling the copper-salt $Cu^6Pt^5Cy^{11}$ in excess with solution of carbonate of soda. Forms large colourless crystals isomorphous with those of carbonate of soda. It is soluble in water. When heated to 100°, it gives off 19·35 p. c. (21 At.) water, becoming white and opaque; at 120°, it gives 2·21 p. c. (7 At.) more; the total quantity of water of crystallization is, therefore, 28 At. (Quadrat, *Ann. Pharm.* 63, 170.)

Anhydrous.			Quadrat.	*Crystallized.*			Quadrat.
6 Na	139·2	15·13	14·76	6 Na	139·2	11·96	
5 Pt	495·0	53·79	53·72	5 Pt	495·0	42·23	
11 Cy	286·0	31·08		11 Cy	286·0	24·40	
				28 Aq	252·0	21·41	21·56
NaCy,5NaPtCy^2	920·2	100·00		+ 28Aq.	1172·2	100·00	

Platinocyanide of Barium. BaCy,PtCy.—Prepared by boiling the corresponding copper-salt with caustic baryta, and separating the excess of baryta by a stream of carbonic acid gas. Six-sided prisms, belonging to the oblique prismatic system, with terminal faces. Colour deep lemon-yellow. The crystals exhibit a violet-blue iridescence on the prismatic faces, and appear yellowish green by transmitted light in the direction of the axis. They are more soluble in hot water than in cold; at 140°, they assume an orange colour, inclining to brown, afterwards becoming green, and ultimately white. They contain 15·3 p. c. water (between 4 and 5 At.); the whole of which is given off at 180°. (Quadrat, *Ann Pharm.* 70, 304.)

	Dried at 180°.		Quadrat.
Ba	68·6	31·24	31·25
Pt	99·0	45·08	44·70
2 Cy	52·0	23·68	
BaCy,PtCy	219·6	100·00	

Platino-platinidcyanide of Barium. $Ba^6Pt^5Cy^{11}$=BaCy,5BaPtCy^2.—Formed by boiling the copper-salt $Cu^6Pt^5Cy^{11}$ with caustic baryta. Rhombic prisms with angles of 100° and 80°, permanent in the air; 1 pt. of the salt requires 33 pts. of water at 16° to dissolve it; but it dissolves readily in boiling water, and crystallizes out on cooling. The crystals contain 14·82 p. c. (22 At.) water of crystallization, of which 7·73 p. c. (12 At.) go off at 100°, and the remaining 6·98 p. c. (10 At.) at 140°. (Quadrat, *Ann. Pharm.* 63, 172.)

	Dried at 140°.		Quadrat.
6 Ba	411·6	34·51	34·5
5 Pt	495·0	41·50	41·1
11 Cy	286·0	23·99	
$Ba^6Pt^5Cy^{11}$	1192·6	100·00	

Platino-platinidcyanide of Strontium.—Preparation similar to that of the barium-salt. Crystallizes in yellow laminæ, which, when heated, become blue-green and ultimately blood-red. When triturated, they yield a brown-red powder. (Quadrat, *Ann. Pharm.* 63, 178.)

Platinocyanide of Calcium. CaCy,PtCy.—Preparation similar to that of the corresponding barium-compound. Thin hemiprismatic needles which exhibit a trichroism similar to that of the barium-salt, appearing lemon-yellow and siskin-green by transmitted, and bluish with a diamond lustre by reflected, light. They are soluble in water. At 100°, they turn red-brown, and afterwards blue. At 180°, they give off 20·38 p. c. of water of crystallization, and assume a yellow colour. (Quadrat, *Ann. Pharm.* 70, 303.)

	Dried at 180°.		Quadrat.
Ca	20	11·7	11·56
Pt	99	57·9	57·55
2 Cy	52	30·4	
CaCy,PtCy	171	100·0	

Platinocyanide of Calcium with Chloride of Calcium.—On mixing a solution of this salt with excess of chloride of calcium, and evaporating, clear, shining, six-sided prisms are obtained, of a pale greenish yellow colour, but exhibiting a deep siskin-green colour by light transmitted along the axis; the prismatic faces have a light-blue colour and diamond lustre. (Quadrat.)

Platino-platinidcyanide of Calcium. $Ca^6Pt^5Cy^{11}$.—Preparation similar to that of the barium-salt. Yellowish green scales, easily soluble in water. Begins to give off its water at 100°, becoming first rose-coloured, then reddish white, and ultimately quite white. At 140°, it gives off 20·44 p. c. (27 At.) water. (Quadrat, *Ann. Pharm.* 63, 174.)

	Dried at 140°.		Quadrat.
6 Ca	120	13·32	13·0
5 Pt	495	54·94	54·7
11 Cy	286	31·74	
$Ca^6Pt^5Cy^{11}$	901	100·00	

Platinoplatinidcyanide of Calcium with Chloride of Calcium?—On evaporating a solution of this salt with excess of chloride of calcium, and leaving the solution to cool, green crystals separate out, which are very soluble in water, and deliquesce in the air. When dried at 100°, they assume a deep red colour with a tinge of blue. (Quadrat.)

Platinocyanide of Magnesium. MgCy,PtCy.—Prepared in the same manner as the salt $Mg^6Pt^5Cy^{11}$ (*vid. inf.*), rectified spirit being used instead of a mixture of ether and alcohol. The crystals thus obtained present considerable variety of colour. When strong alcohol is used, colourless, transparent needles make their appearance at the beginning of the crystallization; but as the alcohol evaporates, they become sulphur yellow,

and are finally converted into flesh-coloured crystals. During the crystallization, a small quantity of a brownish substance separates out. A hot saturated aqueous solution of the salt deposits blood-red crystals on cooling. Crystalline form the same as that of the salt $Mg^6Pt^5Cy^{11}$. When heated, it assumes a sulphur-yellow colour, which afterwards changes to brown.

	Dried at 280°.		Quadrat.
Mg	12	7·37	7·71
Pt	99	60·73	60·07
2 Cy	52	31·90	
MgCy,PtCy	163	100·00	

Platino-platinidcyanide of Magnesium. $Mg^6Pt^5Cy^{11}$ (Quadrat.) $MgCy,PtCy^2$? (Gm.).—1. When a solution of the barium-salt $Ba^6Pt^5Cy^{11}$ is mixed with excess of sulphate of magnesia, sulphate of baryta separates out, and the liquid is found to contain, in addition to the excess of sulphate of magnesia, the magnesium-salt corresponding to the barium-salt used. The sulphate of magnesia may be completely separated by evaporating to dryness, and exhausting with a mixture of alcohol and ether. The alcoholic solution, when slowly evaporated, yields very finely developed crystals.—2. A quicker mode of preparation is to decompose the potassium-salt with sulphate of magnesia, evaporate to a dry powder, digest in alcohol and ether, and evaporate the resulting solution. (Quadrat, *Ann. Pharm.* 63, 175.) ¶

Delicate red square prisms, which in certain directions, exhibit a magnificent greenish yellow metallic lustre, and by transmitted light, appear carmine-coloured in the direction of the axis, and blood-red at right angles to it. (Haidinger, *Pogg.* 68, 302.) The crystals, when crushed with a smooth knife on a perfectly smooth specular surface, yield a carmine-coloured powder, which also presents a smooth mirror-like surface; and this smooth surface, viewed by the dichroscopic lens, exhibits in the lower image an azure-blue colour, which immediately disappears on moistening the powder with water. After the evaporation of the water, there remains a green shining metallic film, which appears carmine-coloured by transmitted light, and when examined by the dichroscope, yields a lower image of a yellow-green, and an upper of bluish green colour with metallic lustre. The aqueous solution of these crystals is colourless. (Gottlieb. *ibid.*)—¶ 1 pt. of the crystals dissolves in 3·4 pts. of water at 16°; the solution is nearly colourless, having only a faint yellowish tinge. A few drops of the solution evaporated quickly on a watch-glass leave a green film, having a metallic lustre, and appearing red by transmitted light. At 35°, the crystals change colour, becoming pale yellow, but retaining their form; at 100° the yellow changes to white. On slightly moistening them after this change, the surface regains its metallic lustre, and the body of the crystals becomes red. The crystals contain 33·26 p. c. (19 At.) water of crystallization, of which 18·69 p. c. (11 At.) goes off at 100°. (Quadrat.)

	Anhydrous.		Quadrat.
6 Mg	72	8·44	8·7
5 Pt	495	58·03	57·8
11 Cy	286	33·53	33·2
$Mg^6Pt^5Cy^{11}$	853	100·00	99·7

The author remarks that, according to the play of colours exhibited by this salt, it appears to correspond to Knop's sesquicyanide of platinum and potassium.

Platino-platinidcyanide of Aluminum.—Obtained by mixing the solution of the potassium-salt with sulphate of alumina, evaporating to dryness, digesting in very strong alcohol (which leaves undissolved the sulphate of potash and the excess of sulphate of alumina), and evaporating; the salt then crystallizes in yellow crystals arranged in stellate groups. They deliquesce very readily, assuming at the same time a green colour. At 100°, they turn red-brown, and when more strongly heated, burn like tinder. ¶

The solution of platinocyanide of potassium forms a white pulverulent precipitate with *Bismuth-salts;* a scanty white precipitate with *Zinc-salts; Stannous* and *Stannic salts;* none with *Lead-salts;* a copious bluish white with *Ferrous* salts; brown-red after a while with *Ferric* salts; and a very copious greenish blue precipitate with *Cupric salts.* (Gm.)

The solution of platinidcyanide of potassium forms a greenish white precipitate with *Cupric salts.* (Knop.)

Platinocyanide of Zinc with Ammonia. $NH^3+ZnCy,PtCy+HO$.—Aqueous chloride of zinc, supersaturated with ammonia, yields with platinocyanide of potassium, large crystals of a very pale greenish yellow colour. They effloresce slightly over oil of vitriol; decompose in the air even below a red heat, burning slowly away with a slight fume, and leaving 67·6 p. c. of a mixture of zinc-oxide and platinum. (Knop & Schnedermann.)

¶ *Platino-platinidcyanide of Lead.* $Pb^6Pt^5Cy^{11}$—Formed by mixing the corresponding potassium-salt with acetate of lead. Yellowish white precipitate; somewhat soluble in boiling water, and leaving a yellowish red saline mass on evaporation. (Quadrat, *Ann. Pharm.* 63, 182.)

Platino-platinidcyanide of Iron. $Fe^6Pt^5Cy^{11}$—Precipitated from a mixture of *ferric chloride* and excess of platino-platinidcyanide of potassium, in flesh-coloured flocks which become brownish when dry. Becomes partially green when exposed to the action of the air. (Quadrat.) ¶

Platinocyanide of Cobalt with Ammonia. $NH^3+CoCy,PtCy$.—From a solution of chloride of cobalt in a mixture of caustic ammonia and carbonate of ammonia, platinocyanide of potassium throws down a flesh-coloured crystalline powder. This powder gives off a small quantity of ammonia at 100°; a few units per cent. at 160°; assumes a fine blue colour and gives off more ammonia at a stronger heat; and burns away slowly with a glimmering light at an incipient red heat, leaving 64·22 per cent. of a mixture of platinum and cobaltoso-cobaltic oxide. (Knop & Schnedermann.)

Platinocyanide of Nickel with Ammonia.—a. Dry. $NH^3+NiCy,PtCy$.—A dilute mixture of the ammoniacal solution of hydrated oxide of nickel and excess of platinocyanide of potassium, deposits in 12 hours, the hydrated compound *b* in needles; the colourless mother-liquor, mixed with excess of the ammoniacal solution of nickel-oxide, deposits the anhydrous compound as a pale violet, granular-crystalline powder, which assumes a bright red colour when heated, and then burns away, leaving 68·35 p. c. of a mixture of platinum and oxide of nickel.

b. Hydrated, $NH^3+NiCy,PtCy+HO$,—Violet needles which, when ignited, leave 66·04 p. c. of nickel oxide and platinum. (Knop & Schnedermann.)

¶ *Platinocyanide of Copper.* $CuCy,PtCy$.—Obtained by mixing

sulphate of copper with platinocyanide of potassium, in the form of a light green precipitate, which resembles the salt $Cu^6Pt^5Cy^{11}$ in nearly all its properties. It is soluble in ammonia, and the solution yields blue crystals. If a recently prepared copper-salt be used, the solution yields large, thick, azure-coloured crystals; but if the copper-salt be dry, delicate needles are obtained, the blue colour of which resembles that of the corn-flower. The former appear to be richer in ammonia than the latter (*vid. inf.*) (Quadrat, *Ann. Pharm.* 70, 307.)

			Quadrat.
Cu	32	17·48	17·30
Pt	99	54·09	54·67
2 Cy	52	28·43	28·03
CuCy,PtCy	183	100·00	100·00 ¶.

Platinocyanide of Copper with Ammonia.—*a.* $NH^3 + CuCy,PtCy,HO$.—A mixture of aqueous platinocyanide of potassium and nitrate of copper supersaturated with ammonia yields, after a few hours, a crop of dark blue needles, which, when left over oil of vitriol, quickly become light blue; at 140°, they give off 11·94 per cent. of water and ammonia, and become green. (Knop & Schnedermann.)

Crystallized.			Knop & Schned.
Cu	32	15·31	15·14
Pt	99	47·37	46·60
2 Cy	52	24·88	
NH^3	17	8·13	11·94
HO	9	4·31	
$NH^3 + CuCy,PtCy + Aq$	209	100·00	

¶ *b.* $2NH^3 + CuCy,PtCy,HO$?—When platino-platinidcyanide of copper is digested in ammonia and the solution left to evaporate, splendid blue crystalline needles are obtained, very soluble in water, alcohol and ether. When exposed to the air, they gradually give off water and ammonia, assuming more and more of a green tint, being ultimately converted into platino-platinidcyanide [or platinocyanide ?] of copper. Acids decompose the compounds, precipitating the copper-salt. (Quadrat, *Ann. Pharm.* 63, 180.)

			Quadrat.
Cu	32	14·16	13·55
Pt	99	43·80	43·90
2 Cy	52	23·01	23·90
2 NH^3	34	15·05	14·31
HO	9	3·98	4·56
$2NH^3,CuCyPtCy,HO$	226	100·00	100·22

The analytical results not agreeing very closely with the formula, the composition of this substance must for the present be regarded as doubtful.

Platino-platinidcyanide of Copper. $Cu^6Pt^5Cy^{11}$—When sulphate of copper is added in excess to an aqueous solution of the potassium salt, $K^6Pt^5Cy^{11}$, a light green precipitate is formed, from which the precipitant is easily removed by washing. On drying this precipitate, the colour changes to dark green. The copper-salt thus obtained is insoluble in water both warm and cold, also in concentrated hydrochloric and in dilute nitric acid. It is decomposed by the fixed alkalis and earths and

their carbonates, the alkali-metal taking the place of the copper, and forming the corresponding salt (*vid. sup.*). It combines with ammonia. (Quadrat, *Ann. Pharm.* 70, 179.)

			Quadrat.
6 Cu	192	19·73	19·4
5 Pt	495	50·87	50·7
11 Cy	286	29·40	
$Cu^6Pt^5Cy^{11}$	973	100·00	

When this salt is treated with sulphuretted hydrogen, sulphide of copper is precipitated, hydrocyanic acid escapes, and a hydroplatinocyanic acid, $HPtCy^2$, remains in solution (p. 44).

$$Cu^6Pt^5Cy^{11} + 6HS = 6CuS + HCy + 5HPtCy^2.$$

Quadrat regards this decomposition as a proof that the composition of the copper-salt is really $CuCy + 5CuPtCy^2$, and that the corresponding salts of the other metals have a similar constitution. (*Ann. Pharm.* 70, 180.) In a subsequent memoir (*Ann. Pharm.* 65, 249), he states that hydroplatinocyanic acid thus prepared, and likewise all the salts obtained from it, contain a sulphocyanogen compound, and consequently yield a blood-red colour with ferric salts. Still more recently (*Ann. Pharm.* 70, 301) he contradicts this statement, and says that the hydroplatinocyanic acid may be obtained by this process absolutely free from any sulphocyanogen compound. ¶

Platinocyanide of Mercury. HgCy,PtCy.—Platinocyanide of potassium forms with mercurous nitrate a thick smalt-blue precipitate (Gm.) This precipitate, the formation of which is attended with a slight evolution of nitrous gas, is a compound of platinocyanide of mercury with mercurous nitrate, which latter salt cannot be extracted by washing with cold water containing nitric acid; but boiling with pure water removes it and leaves the white compound HgCy,PtCy. By digestion for a few hours with a cold solution of mercurous nitrate, this substance may be reconverted into the blue compound; but when boiled with the same solution, it again becomes white, and remains so till the water is evaporated, whereupon the residue first acquires a blue, and then at a stronger heat a brick-red colour. (Döbereiner.)

The *white* compound heated in a tube is resolved into cyanogen gas, mercury, and about 48 per cent. of cyanide of platinum; heated on a plate, it burns with incandescence, but without deflagration, and leaves 38 per cent. of spongy platinum, possessing great inflaming power. By sulphuretted hydrogen it is converted into sulphide of mercury and hydroplatinocyanic acid. It dissolves in hot hydrochloric acid, without evolution of nitrous or hydrocyanic acid, forming a nearly colourless liquid, which is precipitated yellow by potash [and perhaps therefore contains a mixture of corrosive sublimate and hydroplatinocyanic acid], and when evaporated to dryness, leaves a residue, coloured here and there with yellow, red, and blue; this residue, when strongly heated, is resolved into corrosive sublimate, hydrocyanic acid, and protocyanide of platinum. —Potash-ley or baryta-water separates mercuric oxide, and forms a solution of platinocyanide of potassium or barium. (Döbereiner.)

The *blue* precipitate, when strongly heated on a plate, deflagrates with sparkling and a hissing noise. It dissolves in hot hydrochloric acid, with evolution of nitrous and hydrocyanic acid, and forms a nearly colourless liquid, not precipitated either by sal-ammoniac or by alcohol. Treated with aqueous solutions of the fixed alkalis, it leaves a mixture of mercurous and mercuric oxide. (Döbereiner, *Pogg.* 37, 545; also *Ann. Pharm.* 17, 250.)

Platinidcyanide of potassium also forms with mercurous nitrate a dark blue precipitate (Knop) which appears to be identical with the preceding.

With corrosive sublimate, platinocyanide of potassium forms a white precipitate (Gm.); and platinidcyanide of potassium forms a white precipitate with mercuric salts. (Knop.)

¶ According to Quadrat, (*Ann. Pharm.* 63, 183), platinoplatinidcyanide of potassium forms with mercurous nitrate a *white* precipitate, containing $Hg^6Pt^5Cy^{11}$, and a *blue* compound consisting of this salt combined with mercurous nitrate; but these precipitates appear to be similar in all their properties to those above described, and probably agree with them in composition. No satisfactory analysis could be made of them on account of their great proneness to decomposition. The white compound unites with ammonia, forming a crystalline salt. ¶

Platinocyanide and *Platinidcyanide of Silver?*—Platinocyanide of potassium forms with nitrate of silver a white, curdy precipitate, which does not blacken on exposure to light. (Gm.) Platinidcyanide of potassium also yields a white precipitate with silver-solution. (Knop.)

¶ Platinocyanide of silver is also formed by mixing a solution of platinocyanide of diplatosammonium (p. 45) with nitrate of silver. The white precipitate resembles cyanide of silver in appearance, and like that substance is soluble in ammonia. On adding sulphide of ammonium to the ammoniacal solution, sulphide of silver is precipitated, and platinocyanide of ammonium remains in solution. On boiling the platinocyanide of silver with potash, a black precipitate is formed containing all the silver; and the colourless solution, when evaporated, yields long needles of platinocyanide of potassium. (Buckton.)

			Buckton.
2 Cy	52·0	20·08	
Pt	99·0	38·22	38·29
Ag	108·0	41·70	41·71
AgCy,PtCy	259·0	100·00	

Platinoplatinidcyanide of potassium also forms with nitrate of silver a white precipitate which is insoluble in water, does not blacken by exposure to light, and forms a crystalline compound with ammonia. (Quadrat, *Ann. Pharm.* 63, 182.) ¶

Platinocyanide of Silver with Ammonia.—$NH^3 + AgCy,PtCy$.—An aqueous mixture of platinocyanide of potassium with carbonate or nitrate of silver dissolved in ammonia, deposits in a few hours colourless or very pale flesh-coloured needles. When heated, they assume a yellow colour, give off ammonia and cyanogen, and finally leave a residue of silver and platinum. When subjected to the action of a current of chlorine gas, they do not alter their form, but change in colour to green, blue, and finally black; only a small portion however is decomposed by this action. They are insoluble in water, and dissolve but slowly in a large quantity of aqueous ammonia. Strong mineral acids at a boiling heat neither dissolve nor decompose them. (Knop and Schnedermann.)

			Knop & Schned.
NH^3	17	6·16	7·10
Ag	108	39·13	39·02
Pt	99	35·87	35·40
2 Cy	52	18·84	18·76
$NH^3 + AgCy,PtCy$	276	100·00	100·28

PROTOCYANIDE OF PALLADIUM. PdCy.—1. Formed by boiling protoxide of palladium with aqueous cyanide of mercury. (Wollaston).—2. By precipitating a palladious salt with cyanide of mercury; if the solution be dilute, the precipitate does not form till after some time. (Wollaston.)—If excess of acid be present, no precipitate is formed. (Berzelius.)

Pale yellowish white powder. (Wollaston).—Leaves palladium when heated to redness.—Cyanide of palladium precipitated according to (2) from palladious nitrate, detonates like gunpowder when heated (Wollaston); an effect which, according to Berzelius, is due to the presence of palladious nitrate in a state of combination.

Bicyanide of Palladium. $PdCy^2$.—Chloropalladiate of potassium (VI, 354) stirred up with water and mixed with cyanide of mercury, yields a pale rose-coloured, flocculent precipitate, which, however, gradually assumes a brighter hue, emitting at the same time an odour of hydrocyanic acid. (Berzelius, *Pogg*, 13, 461.)

Protocyanide of Palladium with Ammonia, NH^3,PdCy.—1. The solution of a palladious salt in ammonia, evaporated till it gives off the excess of ammonia, but not till it assumes a yellow colour, yields with cyanide of mercury, after a few seconds, colourless, pearly, crystalline scales. (Berzelius, *Pogg*, 13, 460.) (Formerly regarded as cyanide of palladium.) —2. Protocyanide of palladium dissolves with evolution of heat in aqueous ammonia, only an inconsiderable quantity of flocculent matter being left behind. From the solution, the compound crystallizes abundantly in needles. 79·3 pts. (1At.) of cyanide of palladium absorb in two days only 11·3 pts. (about ⅔ At.) of dry ammoniacal gas.—The needles in the dried state undergo no change at 120°.—When heated with water, they dissolve partially, giving off a trace of ammonia, and separate out again as the solution cools. They dissolve readily in ammonia, from which solution they are separated unchanged on the addition of warm hydrochloric acid; but an excess of hydrochloric acid precipitates cyanide of palladium. (Fehling, *Ann. Pharm.* 39, 119.)

		Fehling.
Pd	53·3	54·78
Cy	26·0	
N	14·0	
H^3	3·0	3·22
NH^3,PdCy	96·3	

Palladiocyanide of Potassium. KCy,PdCy.—The solution of protocyanide of palladium in aqueous cyanide of potassium, filtered and evaporated, yields transparent, colourless, thin rhombic prisms, having the angles of their lateral edges equal to 108° and 72°, often truncated at the acute lateral edges, whereby four dihedral angles of 126° are produced. The crystals decrepitate when gently heated, and then fuse with intumescence. (Gm. *Handb.* Aufl. 2, 2, 1693.)—The salt crystallizes, sometimes in transparent and colourless laminæ, which when heated for some time to 200°, give off 6·14 p. c. (1 At.) of water, sometimes in prisms, which quickly effloresce on the surface, and at 150° give off 17·64 p. c. (3 At,) of water.

	Dehydrated.		Rammelsberg.
K	39·2	27·13	27·74
Pd	53·3	36·88	36·16
2 Cy	52·0	35·99	
KCy,PdCy	144·5	100·00	

Hydro-iridiocyanic Acid.—Analogous to hydroplatinocyanic acid. (Döbereiner, *Pogg*, 37, 548.)

Iridiocyanide of Potassium.—By gently igniting a mixture of ferrocyanide of potassium and pulverized iridium for some time in a glass flask, exhausting the calcined mass with hot water, filtering to remove charcoal, iron, and metallic iridium, and evaporating, crystals of ferrocyanide of potassium are first obtained, and afterwards crystals of the iridium-salt.

Transparent, colourless, four-sided prisms, generally united as macle-crystals, with re-entering angles at the terminal faces. The crystals are anhydrous, decrepitate strongly when heated, turn black, and when more strongly heated fuse, with separation of iridium, which often coats the glass vessel with a metallic mirror. They dissolve readily in water, but are insoluble in alcohol. Hydrochloric acid does not form any precipitate in the aqueous solution. (Wöhler & Booth, *Pogg*, 31, 167.)

The salt is imperfectly decomposed by ignition in contact with the air, by evaporation with aqua-regia, and by exposure to a stream of chlorine gas. In a current of hydrochloric acid gas, it becomes heated, and assumes a greyish green colour; but even when the passage of the gas is continued for a long time, the decomposition which takes place is very imperfect; and on subsequently passing hydrogen gas over the compound at an elevated temperature, a large quantity of ammonia is formed, and water subsequently dissolves out the unaltered salt, an odour of hydrocyanic acid being at the same time emitted. The green colouring produced by hydrochloric acid gas, as well as by chlorine and aqua-regia, is probably due to the formation of protochloride of iridium, and favours the supposition that the salt contains *proto*cyanide of iridium.—The salt is anhydrous. Its aqueous solution forms with mercurous nitrate a yellowish white precipitate, which when ignited in a retort leaves a grey powder, probably protocyanide of iridium, which turns black when ignited in the air. (Rammelsberg, *Pogg*, 42, 139.)

	Crystallized.			Rammelsberg.
2 K	78·4	....	30·69	32·89
Ir	99·0	....	38·77	35·60
3 Cy	78·0	....	30·54	
2KCy,IrCy	255·4	....	100·00	

¶ Cyanide of Methyl. $C^2H^3,C^2N = C^4H^3N$.—*Preparation.* 1. By distilling dry sulphomethylate of potash with cyanide of potassium, adding chloride of calcium to the distillate, and distilling again at a gentle heat. The product is contaminated with hydrocyanic acid. (Frankland & Kolbe, *Chem. Soc. Mem.* 3, 386; *Ann. Ch. Pharm.* 65, 288.)—2. By the action of cyanide of potassium on sulphate of methyl. The product is contaminated with cyanide of ammonium and formiate of ammonia; the latter impurity imparts to the product an intolerable taste and odour, and a highly poisonous action; it may be removed by boiling with mercuric oxide and then with anhydrous phosphoric acid. (Dumas, Malaguti, & Leblanc, *Compt. rend.* 25, 474.)—3. By distilling a mixture of anhydrous phosphoric acid and crystallized acetate of ammonia:

$$C^4{}^{H^3}_{NH^4}O^4 = C^4H^3N + 4HO.$$

The product is purified by digestion with a saturated solution of chloride

of calcium, and rectification over solid chloride of calcium and magnesia. (Dumas, *Compt. rend.* 35, 383.)

Colourless liquid which boils at 77°, and mixes with water in all proportions.

Calculation.				Or:			
4 C	24	....	58·53	C^2H^3	15	....	36·60
3 H	3	....	7·32	C^2N	26	....	63·40
N	14	....	34·15				
C^2H^3,C^2N	41	....	100·00		41	....	100·00

	Vol.		Density.	Or:			
C-vapour	4	....	1·6640	Methyl-gas	1	....	1·0399
H-gas	3	....	0·2079	Cyanogen-gas	1	....	1·8026
N-gas	1	....	0·9706				
Vapour	2	....	2·8425	Vapour	2	....	2·8425
	1	....	1·4212		1	....	1·4212

Might also be regarded as *Acetonitryl*, C^4H^3,N.

Cyanide of methyl boiled with aqueous potash gives off ammonia and forms acetate of potash. (Frankland & Kolbe; Dumas, Malaguti & Leblanc.)—Chromic acid and boiling nitric acid have no action upon it. Potassium acts violently on it even in the cold, producing rise of temperature; cyanide of potassium is formed, and a combustible gaseous mixture evolved, consisting of free hydrogen and carburetted hydrogen. (Dumas.) ¶

Cyanic Acid. C^2NH,O^2.

WÖHLER. *Gilb.* 71, 95; 73, 157.—*Pogg*, 1, 117; 5, 385.—*Ann. Pharm.* 45, 351.

LIEBIG. *Kastn. Arch.* 6, 145.—*Schw.* 48, 376.—*Pogg*, 15, 561 and 619.

LIEBIG & WÖHLER. *Pogg*, 20, 369; also *Mag. Pharm.* 33, 137.

Originally distinguished by the name of *Cyanous acid*. First noticed by Vauquelin in 1818; afterwards more definitely prepared and examined by Wöhler in 1822.

Formation. Cyanate of potash is produced when carbonate of potash is ignited in a current of cyanogen gas, or when the same salt is ignited in contact with cyanide of mercury. (Wöhler.)—2. An alkaline cyanate is formed on saturating the aqueous solution of a fixed alkali with cyanogen gas. (Wöhler, VII. 387.)—3. Cyanic acid is formed, as first observed by Gay-Lussac, on bringing cyanogen in contact with peroxide of lead. (Döbereiner.)—4. Cyanate of potash is formed on heating a mixture of dry ferrocyanide of potassium and peroxide of manganese in contact with the air. (Wöhler.)—5. Also on heating nitre with ferrocyanide of potassium or cyanide of mercury, or on igniting a mixture of nitre and excess of blood-charcoal. (Wöhler.)—6. Also when cyanide of potassium is fused with litharge. (Liebig, *Ann. Pharm.* 41, 289.)—7. Also when melam or ammelin (the latter somewhat in excess) is fused with hydrate of potash. (Liebig, *Pogg.* 34, 584.)—8. Vapour of cyanic acid is evolved when mercuric urate is heated to redness (Wöhler), or when uric acid is heated with peroxide of manganese and oil of vitriol.

(Döbereiner, *Gilb.* 74, 121.)—9. In the distillation of cyanuric acid, $C^6N^3H^3O^6$, an atom of that compound splitting up into 3 atoms of cyanic acid. (Wöhler.)—10. In the decomposition of urea by nitrate of silver. (Liebig, VII, 369.)

Preparation. 1. Cyanuric acid, previously dehydrated, is heated in a small retort to commencing redness, and the vapour of cyanic acid condensed in a receiver surrounded with a freezing mixture. (Wöhler, *Pogg.* 15, 623; Liebig and Wöhler, *Pogg.* 20, 383).—2. Dry hydrochloric acid gas is passed over dry cyanate of silver, and the vapour of cyanic acid thereby evolved is passed from the tube into a cooled receiver. If too much hydrochloric acid gas be passed through the tube, the cyanic acid is decomposed, yielding sal-ammoniac and carbonic acid gas. (Wöhler, *Pogg.* 5, 386.)

Properties. Cyanic acid prepared by (1) is a thin, colourless liquid; reddens litmus strongly; has an extremely pungent odour, like that of glacial acetic acid, and somewhat like that of sulphurous acid. The vapour excites a copious flow of tears, and causes violent smarting in the hands. A drop of the liquid acid instantly produces a white blister, attended with severe pain. (Liebig and Wöhler, *Pogg.* 15, 623; 20, 383.)

Calculation, according to Wöhler's Analysis of Cyanate of Silver.

2 C	12	27·91
N	14	32·56
H	1	2·32
2 O	16	37·21
C^2NH,O^2	43	100·00

According to this view, cyanic acid is an acid aldide of the nucleus hydrocyanic acid; the radical-theory regards it as a *Hydrate of Cyanic acid*, HO, CyO; that is to say, as a compound of a hypothetically anhydrous cyanic acid, Cy O, with 1 At. basic water.

Decompositions. 1. The acid in the free state changes spontaneously into cyamelide (insoluble cyanuric acid) a substance which is polymeric with it, the change taking place the more quickly, and with less rise of temperature, in proportion as the substance is less cooled. At 0°, the acid changes in an hour, and without explosion, into dry, hard, snow-white cyamelide; but, if it be removed from the frigorific mixture, so that it may assume the ordinary temperature, it soon becomes turbid and milky, begins to boil, thickens to a pasty consistence, and becomes continually hotter, till it explodes; the paste is then scattered about, and changes completely into cyamelide. At ordinary temperatures, the conversion is complete in five minutes; it likewise takes place as quickly under increased external pressure as under the ordinary pressure. Vapour of cyanic acid mixed with an inactive gas appears to remain unchanged for a long time. (Liebig and Wöhler.)—2. The acid, mixed with water, splits up spontaneously in a short time, at ordinary temperatures, into 2 At. carbonic acid and 1 At. ammonia, the acid reaction of the liquid then changing to an alkaline reaction, and a smell of ammonia being produced. (Wöhler.)

$$C^2NHO^2 + 2HO = 2CO^2 + NH^3.$$

Whilst one portion of the cyanic acid is thus converted into bicarbonate of ammonia, another portion takes up the ammonia, driving out the carbonic acid with effervescence, and forms cyanate of ammonia, which, on evaporation, is converted into urea; and a third part of the acid is converted into cyamelide, and separates in white flakes. This decomposition is likewise attended with evolution of heat. (Liebig and Wöhler.) The aqueous acid, when prepared by bringing cyanic acid vapour in contact with ice, in a receiver surrounded with ice, remains nearly unaltered at the temperature of 0°, giving off but a few bubbles of carbonic acid. (Liebig and Wöhler.) A considerable quantity of water retards the decomposition of the acid into carbonic acid and ammonia; the presence of one of the stronger acids accelerates it, by virtue of the affinity of that acid for the ammonia. (Wöhler.) — 3. Sulphuretted hydrogen exerts a decomposing action on the aqueous acid. (Liebig.)

Combinations. A. With *Water.—Aqueous Cyanic acid.*—Cyanic acid vapour is very rapidly absorbed by water and by ice, the latter melting during the absorption. The aqueous acid may therefore be obtained by passing the vapour evolved on heating cyanuric acid or thoroughly dried cyanate of silver (p, 62), into a small quantity of water or ice, contained in a vessel surrounded with ice; or, by diffusing cyanate of silver in ice-cold water, passing into the liquid a quantity of sulphuretted hydrogen not sufficient to decompose the whole or the cyanate, the liquid being stirred all the while, and filtering quickly. (Liebig). This aqueous acid is transparent and colourless, reddens litmus, tastes sour, and exhales a very pungent odour of cyanic acid. It soon changes into carbonic acid and ammonia, the change being, however, slower, as the liquid is colder and more dilute.

B. With *Hydrochloric acid. — Hydrochlorate of Cyanic acid.*— C^2NHO^2,HCl, or C^2AdCl,O^2. When dry hydrochloric acid gas is passed through a long tube containing well dried cyanate of potash, great heat is produced, and a colourless liquid distils over. This reaction is always accompanied by the production of cyamelide, which remains behind on dissolving the chloride of calcium in water; and, if the cyanate of potash be not kept cool, we obtain, instead of the above-mentioned distillate, nothing but a mixture of cyamelide and hydrochloric acid. Cyanate of silver appears to be better adapted for the preparation than the potash-salt. (Wöhler). [But Liebig prepares cyanic acid with hydrochloric acid and cyanate of silver. (p. 62.)]

Transparent and colourless liquid, which fumes strongly in the air, and smells very strongly of cyanic and hydrochloric acid.

				Wöhler.	
C^2NHO^2	43·0	54·16			
H	1·0	1·26			
Cl	35·4	44·58	44·04		45·0
C^2NHO^2,HCl	79·4	100·00			

Wöhler, before analysing the compound, freed it completely from adhering hydrochloric acid by passing hydrogen over it; hence he found a constant composition.

The liquid, enclosed in a sealed glass tube, remains unaltered at 0°; but, at ordinary temperatures, solidifies in a few days into a crystalline mass, consisting of sal-ammoniac and cyamelide, the solidification being accompanied by the evolution of highly compressed carbonic and hydrochloric acid gases. (Wöhler.) [It is impossible to represent this decomposition

by an equation, unless we suppose that water takes part in it.] The compound, heated in open vessels, is resolved into cyamelide and hydrochloric acid gas. It dissolves immediately in water, yielding a solution of sal-ammoniac, with great rise of temperature and violent evolution of carbonic acid gas:

$$C^2NHO^2,HCl + 2HO = NH^4Cl + 2CO^2.$$

Hence it immediately begins to effervesce when exposed to moist air, or when breathed upon, the decomposition going on till nothing remains but a solid mass of sal-ammoniac. When mixed with alcohol, it decomposes immediately, with great evolution of heat, into hydrochloric acid and cyanuric ether. (Wöhler, *Ann. Pharm.* 45, 357.) The term *cyanuric ether* is applied by Wöhler to the copulated compound $C^4H^5O,C^6N^3H^3O^3$; hence:

$$2(C^2NHO^2,HCl) + C^4H^5O^2 = C^4H^5O,C^6N^3H^3O^3 - HCl.$$

C. With *Salifiable Bases*, forming salts called CYANATES. These salts are obtained, sometimes by the methods indicated for the formation of cyanic acid, sometimes by bringing the aqueous acid in contact with the base, sometimes by precipitating an aqueous solution of cyanate of potash or baryta with a heavy metallic salt. (Wöhler.) In the last case, however, according to Haidlen and Fresenius, a carbonate is sometimes thrown down instead of the cyanate, *e.g.* with lead and zinc salts.—Many cyanates, as those of silver oxide and mercurous oxide, when heated in the dry state, give off undecomposed cyanic acid, together with carbonic acid and nitrogen gases; others, as those of the fixed alkalis, remain undecomposed even at a red heat, excepting in presence of moisture, by which the salt is decomposed, at a moderate heat, into carbonate of ammonia, carbonate of the fixed alkali, and a substance resembling paracyanogen; the same decomposition is produced even by repeated solution in water and evaporation:

$$C^2NKO^2 + 3HO = KO + NH^3 + 2CO^2.$$

In the current of the voltaic battery, aqueous cyanate of baryta yields nothing but oxygen at the positive pole, while ammonia and carbonate of baryta appear at the negative pole. (Wöhler.) [Can carbonic acid be produced at the negative pole?]—Cyanates detonate when heated with chlorate of potash. (Wöhler.) Oil of vitriol, dilute hydrochloric acid, and aqueous oxalic acid eliminate from cyanates nothing but carbonic acid, retaining the ammonia; crystallized oxalic acid triturated with a cyanate, or concentrated hydrochloric acid, expels the anhydrous acid, which is then converted into cyamelide. Dilute sulphuric acid eliminates, together with the carbonic acid, a quantity of undecomposed cyanic acid vapour, which may be recognized by its intensely pungent odour. Some acids, as acetic acid (and likewise mineral acids, *e.g.*, hydrochloric acid, according to Campbell), if added to the concentrated solution of the potash-salt, likewise throw down crystals of acid cyanurate of potash. (Wöhler.) The odour of cyanic acid is slowly, and therefore most perceptibly evolved, on dissolving cyanate of potash in water containing cream of tartar. (Hünefeld, *Schw.* 60, 477.)—Those cyanates which are soluble in water form white precipitates with nitrate of lead or silver, or with mercurous nitrate, greenish brown with nitrate of copper, and brownish yellow with chloride of gold. (Wöhler.)—They do not form any precipitate with protochloride or bichloride of tin, protochloride or sesquichloride of iron, or with protochloride of mercury.—Mixed with ferrous salts, with addition

of sulphuretted hydrogen or sulphite of ammonia, they do not yield prussian blue. (Wöhler.)

Cyanate of Ammonia ; basic. When the vapour of cyanic acid, evolved by heating cyanuric acid, is passed into dry ammoniacal gas, heat is evolved, and a thick cloud produced, which condenses into a fine, crystalline, woolly, and very bulky mass, or a snow-white powder. Part of the salt, however, fuses and is converted into urea, in consequence of the heat produced in its formation. The salt dissolves readily in water; the solution gives off carbonic and cyanic acids when treated with acids, and ammonia when treated with potash ; nitric acid does not precipitate urea from it. In a vessel filled with ammoniacal gas, it undergoes no change ; but under the following circumstances, it is converted into urea, the change being attended with evolution of ammonia, a proof that the salt is basic. 1. In the course of two days, when the salt covered with paper is exposed to the air. 2. Immediately on fusion. 3. Immediately on boiling the aqueous solution. 4. Gradually when the aqueous solution is left to evaporate spontaneously in the air, or evaporated by heat.—The aqueous solution of cyanate of ammonia may also be obtained by decomposing cyanate of lead with aqueous ammonia, or cyanate of silver with aqueous sal-ammoniac at ordinary temperatures. The filtrate thus obtained likewise leaves urea when evaporated to dryness. (Liebig and Wöhler, *Pogg.* 20, 393.)

CYANATE OF POTASH. C^2NK,O^2.—For the formation of this salt, *vid. Formation of Cyanic acid.* (*p.* 61.)

Preparation. 1. Cyanide of potassium prepared by fusing the ferrocyanide with carbonate of potash (VII. 413), and containing 5 At. cyanide of potassium to 1 At. cyanate of potash, is heated to the melting point in an earthen [or iron] crucible ; [somewhat more than 3 times the quantity] of pulverized and gently ignited litharge is then introduced ; the fused mass being stirred at the same time; the mixture heated till the metallic lead has collected at the bottom ; then poured out ; and the solidified saline mass pulverized and boiled with alcohol as long as the resulting solution continues to yield cyanate of potash on cooling. (Liebig, *Ann. Pharm.* 41. 289) ;

$$C^2NK + 2PbO = C^2NKO^2 + 2Pb.$$

An excellent method (Gm.)—¶ According to Clemm (*Ann. Pharm.* 66, 382), the best mode of preparing cyanate of potash is to add 15 parts of minium, by small portions at a time, to the fused and somewhat cooled, but still fluid mass of 8 pts. ferrocyanide of potassium and 3 pts. carbonate of potash, taking care that the temperature does not rise too high. The crucible is then to be returned to the fire, and the contents stirred, poured out, and left to cool.—¶ 2. A finely-pulverized mixture of ferrocyanide of potassium and peroxide of manganese is raised to a very low red heat (if the heat be stronger, the cyanic acid is decomposed by formation of carbonic acid and protoxide of manganese): (Wöhler). Or an intimate mixture of 1 pt. crystallized ferrocyanide of potassium, and from 1½ to 2 pts. of manganese, is formed into a cone, the point of which is set on fire by a red-hot coal, whereupon a slow combustion extends throughout the mass. (Liebig, *Kastn. Arch.* 38, 108.) Or better : A very finely-pulverized and intimate mixture of 2 pts. dehydrated ferrocyanide of potassium and 1 pt. manganese is heated to low redness on an iron plate, with constant stirring, the mass gradually burning with a

glimmering light. The oxygen of the manganese is far from sufficient for the formation of the cyanate of potash, but the air likewise takes part in the action; if more manganese be used, a considerable quantity of carbonate of potash is produced. (Liebig, *Ann. Pharm.* 38, 108.) — 3. An intimate mixture of 3 pts. dehydrated ferrocyanide of potassium, 1 pt. dry carbonate of potash, and 4 pts. very finely-pounded manganese, is gently ignited in a crucible till a sample dissolved in water after cooling, no longer forms prussian blue with ferric salts. The mass, when cold, is finely pounded and boiled with 80 per cent. of alcohol. (Berzelius, *Lehrb.*) — 4. A mixture of 4 pts. ferrocyanide of potassium and 3 pts. nitre is thrown by small portions into a red-hot crucible. Strong detonation then takes place, and there remains a black mixture of undecomposed ferrocyanide, charcoal, ferric oxide, carbonate of potash, and cyanate of potash, the quantity of the latter amounting to 1 pt. (Wöhler.) — 5. Ferrocyanide of potassium pulverized and well dried is heated nearly to redness in a shallow iron vessel, the fused mass being constantly stirred; the product taken out after a while with an iron scoop, pulverized after solidification, and again fused with agitation. (Campbell, *Ann. Pharm.* 28, 52.) In this process, the oxidation is not produced directly by the oxygen of the air, but by the ferric oxide formed, which gives up its oxygen to the cyanide of potassium, and again takes it up from the air. (Wöhler, *Berzelius Jahresber.* 19, 260.) A considerable quantity of ferrocyanide remains undecomposed, even after several hours' fusion. (*Gm.*) — 6. By deflagrating a mixture of 127 pts. cyanide of mercury and 20 pts. nitre, a mixture is produced containing a large proportion of cyanate of potash, and small quantities of carbonate of potash and cyanide of potassium. (Wöhler.) — 7. A mixture of nitre and excess of blood-charcoal, ignited by a red-hot coal, deflagrates slowly, and leaves a carbonaceous residue containing cyanate of potash. (Wöhler.) — 8. When cyanogen gas is passed over red-hot carbonate of potash, the salt liquefies, gives off gas, turns yellow, and is converted into a mixture of cyanate of potash, cyanide of potassium, and undecomposed carbonate of potash. The same mixture, contaminated however with a substance resembling paracyanogen, is obtained on fusing carbonate of potash with cyanide of mercury. (Wöhler.) — Döbereiner (*Pogg.* 74, 421,) passes the cyanic acid vapours, which are abundantly evolved on heating about 1 At. uric acid (supposed = 90), or ferrocyanide of potassium, [?] with 6 At. oil of vitriol and 3 At. manganese, into alcohol containing potash, from which carbonate and cyanate of potash crystallize out; he then heats the alcohol till the latter salt dissolves, and brings it to the crystallizing point by cooling. — 9. Hydrate of potash heated with an equivalent quantity of melam or with ammelin somewhat in excess, fuses, with violent evolution of ammonia, and yields pure cyanate of potash. (Liebig, *Pogg.* 34, 584.)

To obtain the cyanate of potash in a purer state from the residues of of the processes 1—8, they must be boiled with alcohol of the strength of 86 p. c. as long as the resulting liquid continues to yield cyanate of potash on cooling. The alcoholic mother-liquid serves to repeat the exhaustion of the residue. The crystals must be several times washed with absolute alcohol, pressed, rapidly dried at 100°, or in vacuo over oil of vitriol, and preserved in a well-closed bottle, because the salt is very easily resolved by the action of moisture into ammonia and bicarbonate of potash. (Berzelius.)

Properties. Small colourless laminæ and needles, similar to those of

chlorate of potash. Fuses at a temperature much below redness to a transparent and colourless liquid. Inodorous; tastes like nitre. (Wöhler.)

Crystallized.				Or:				Wöhler.
C^2N	26·0		32·02	KO	47·2		58·43	58·29
K	39·2		48·27	C^2NO	34·0		41·57	41·71
2 O	16·0		19·71					
C^2NK,O^2	81·2		100·00		81·2		100·00	100·00

The dry salt is not decomposed by ignition; but if water be dropped upon it, at that temperature, it is rapidly resolved into carbonate of potash and [carbonate of] ammonia. The same change takes place when an aqueous solution of the salt is evaporated in the air, either at the ordinary or at a higher temperature (Wöhler):

$$C^2NKO^2 + 3HO = KO + NH^3 + 2CO^2.$$

Hydrogen gas passed over the red-hot salt, abstracts all the oxygen and reduces it to cyanide of potassium; but the water thereby produced decomposes another portion of the cyanate of potash into carbonate of potash and [carbonate of] ammonia. (Wöhler.) Charcoal at a red heat likewise converts cyanate of potash into cyanide of potassium. (Gm.) Potassium dissolves quite quietly in melting cyanate of potash, forming a mixture of potash and cyanide of potassium:

$$C^2NKO^2 + 2K = C^2NK + 2KO.$$

Red-hot iron-filings form, with the salt, a mixture of cyanide of potassium, ferrocyanide of potassium, and protoxide of iron. (Wöhler). Sulphur fuses with the salt, forming a mixture of sulphocyanide of potassium, sulphide of potassium, and sulphate of potash. (Wöhler.) In this case, other decomposition-products are probably formed at the same time.—Sulphuretted hydrogen converts the melted salt into a yellow mixture of sulphide and sulphocyanide of potassium, a small quantity of hydrosulphate of ammonia being sublimed at the same time. (Wöhler.) Dry hydrochloric acid gas, passed over the heated salt, produces sal-ammoniac and chloride of potassium. (Wöhler.) Probably also phosgene is formed at the same time:

$$C^2NKO^2 + 4HCl = KCl + NH^4Cl + 2CClO.$$

For the other decompositions which acids produce with cyanate of potash, see the behaviour of cyanates with acids (p. 64).

Cyanate of potash dissolves readily in water, sparingly in cold hydrated alcohol, more easily in boiling hydrated alcohol; in absolute alcohol it is insoluble. (Wöhler.)

Cyanate of Soda.—Crystallizable. (Wöhler.)

Cyanate of Baryta.—1. Cyanogen gas, or the vapour produced by heating urate of mercuric oxide (p. 61, 8), is passed into baryta-water (in the latter case carbonate of baryta is precipitated); the resulting hydrocyanate of baryta decomposed by passing carbonic acid gas through it; the liquid, which has become brown from the presence of paracyanogen, filtered, and the cyanate of baryta precipitated by alcohol (evaporation would give rise to the formation of carbonate of baryta). (Wöhler). [Wöhler having more recently discovered that cyanuric acid is converted by heat into vapour of cyanic acid, he may now perhaps think it better to pass this vapour into the baryta-water.] — 2. Cyanurate of baryta heated to fusion in

a retort is converted into cyanate. (Berzelius.) — 3. Alcohol added to a concentrated aqueous mixture of cyanate of potash and acetate of baryta, throws down cyanate of baryta. (Berzelius, *Lehrb.*)

Colourless silky needles.—The salt ignited with sulphur yields hydrosulphate of ammonia, sulphide of barium, sulphocyanide of barium, and sulphate of baryta. (Wöhler). [Is the hydrogen in the hydrosulphate of ammonia derived from the water of crystallization?]—The aqueous solution of the salt is partially resolved by evaporation into carbonate of baryta and [carbonate of] ammonia. (Wöhler.)

Cyanate of Lime.—Formed by heating urate of mercuric oxide, and passing the resulting vapours into milk of lime. The salt is not crystallizable. (Wöhler.)

Cyanate of Yttria.—A mixture of the alcoholic solutions of cyanate of potash and a salt of yttria, deposits cyanate of yttria after a while in the anhydrous state, and insoluble in water and alcohol. If aqueous solutions be used, the precipitate is formed immediately, but it is then contaminated with carbonate of yttria. (Berlin).

Cyanate of Lead.—Acetate of lead forms, with cyanate of potash, a dense white precipitate, which quickly settles down, and takes the form of slender needles, like chloride of lead. When heated out of contact of air, the precipitate fuses, assumes a reddish hue, and then yields a light green powder, which appears to be a mixture of metallic lead and cyanide of lead. Heated in contact with the air, it takes fire, and is readily reduced, with emission of sparks, to metallic lead. Potash extracts cyanic acid, and separates a reddish yellow crystalline powder. Sulphuretted hydrogen produces sulphide of lead, with separation of cyanic acid, which, by the action of the water simultaneously formed, is quickly resolved into carbonic acid and ammonia. Other acids act on cyanate of lead in the same manner as on cyanate of silver. Boiling water dissolves a small quantity. (Wöhler, *Gilb.* 73, 166.)

Crystallized.				Or:				Wöhler.
C^2N	26	....	17·81	PbO	112	....	76·71	77
Pb	104	....	71·23	C^2NO	34	....	23·29	23
2 O	16	....	10·96					
C^2NPb,O^2	146	....	100·00	PbO,CyO	146	....	100·00	100

Ferrous Cyanate.—This very unstable salt is obtained by treating cyanate of silver with iron and water. (Wöhler.)

Cupric Cyanate.—Cyanate of baryta yields a greenish brown precipitate with nitrate of copper. (Wöhler.)

Mercurous Cyanate.—Cyanate of baryta forms, with mercurous nitrate, a white precipitate which, when heated after washing and drying, gives off partly undecomposed cyanic acid, partly carbonic acid and nitrogen, and leaves a tumefied carbonaceous mass; the precipitate also gives up its acid to potash. (Wöhler.)

Cyanate of Silver.—Formed by precipitating neutral nitrate of silver with cyanate of potash or baryta. After washing and drying, it forms a white anhydrous powder. (Wöhler, *Gilb.* 73, 166; *Pogg.* 1, 120; 5, 385; *Ann. Pharm.* 45, 359.)—Urea evaporated at a gentle heat with aqueous

nitrate of silver, is decomposed, yielding nitrate of ammonia and cyanate of silver, which crystallizes in prisms. (Liebig & Wöhler, *Ann. Pharm.* 26, 301; Werther, VII, 369).

				Or:				Wöhler.
C^2N	26		17·33	AgO	116		77·35	77·24
Ag	108		72·00	C^2NO	34		22·65	22·76
2 O	16		10·67					
C^2NAg,O^2	150		100·00	AgO,CyO	150		100·00	100·00

The dry salt, when strongly heated, turns black, fuses, takes fire with a noise, even if not in contact with the air, and leaves a brownish mass, which, when more strongly ignited, gives off a large quantity of cyanogen and leaves metallic silver. (Wöhler.)—The thoroughly dried salt, when very gently heated in a glass tube, gives off vapour of cyanic acid. (Liebig, *Kastn. Arch.* 6, 149.) [As no water is present, the vapour thus evolved cannot be cyanic acid, C^2NH,O^2; can there be such a compound as C^2NO?]—If a trace of moisture be present, the cyanate of silver gives off a small quantity of carbonate of ammonia, silver being reduced at the same time. When quickly and strongly heated in the perfectly dry state, it takes fire, and gives off a large quantity of gas, containing 17 vol. carbonic acid to 8 vol. nitrogen. There remains a tumefied grey mass which does not give up a trace of silver to dilute nitric acid, evolves cyanogen gas when ignited in the air, but is not wholly converted into pure silver, even by four hours' ignition, inasmuch as a portion withstands the solvent action of the nitric acid. (Liebig, *Kastn. Arch.* 6, 149.)—The perfectly dry salt, when strongly heated, exhibits incandescence, and gives off with violence a very large quantity of gas, the last portions of which contain 10 vol. nitrogen gas to 22 vol. carbonic acid. The proportion of nitrogen in the residue is, therefore, somewhat greater than in cyanogen; and in fact this residue, when burnt with oxide of copper, yields to 100 vol. nitrogen only 137 vol. carbonic acid (instead of 200); it may therefore contain mellonide of silver, since mellon, C^6N^4, would yield 150 vol. carbonic acid gas to 100 vol. nitrogen. (Liebig, *Ann. Pharm.* 50, 358.)—When dry chlorine gas is passed over the dry salt contained in a tube, it is completely decomposed, if sufficiently heated; and there passes into the receiver a transparent and colourless liquid, which fumes in the air, and then becomes white and solid, after which water dissolves but a part of it with effervescence. No cyanic acid or ammonia is obtained in this reaction. (Liebig.) But if moist chlorine gas and moist cyanate of silver be used, a different reaction takes place, attended with great and sudden evolution of heat, and copious white fumes are produced which condense in the receiver to a white flocculent powder, or a crust of cyanuric acid. In one of these experiments, there was produced, instead of cyanuric acid, a white flocculent substance, which had an astringent and somewhat acid taste, did not effervesce with acids, dissolved in water much more readily than cyanuric acid, and was precipitated therefrom in white flakes by ammonia. Similar products are obtained in the decomposition of cyanate of potash by chlorine, but they are always accompanied by some of the last named flocculent, soluble substance. (Liebig, *Pogg.* 15, 561.)—When chlorine gas is passed through water in which cyanate of silver is suspended, bubbles of carbonic acid are evolved, and sal-ammoniac and chloride of silver formed. (Liebig, *Pogg.* 15, 561.)—[These interesting, but not yet perfectly intelligible experiments of Liebig's deserve to be more fully carried out.]—Hydrochloric or

hydrosulphuric acid gas is absorbed, with rise of temperature, by cyanate of silver, chloride or sulphide of silver being formed, and cyanic acid set free; the latter, however, unless the heat be kept down, is immediately converted into cyamelide. (Wöhler.) Dilute nitric acid dissolves the salt immediately, and decomposes it. Any cyanide of silver that may be mixed with it remains unaltered. (Wöhler.) Iron reduces the silver from the salt suspended in water. Aqueous potash abstracts the acid from the salt. (Wöhler.)—Aqueous cyanide of potassium decomposes it, yielding argentocyanide of potassium and cyanate of potash. (Glassford & Napier):

$$C^2NAgO^2 + 2KCy = C^2NKO^2 + KCy,AgCy.$$

Cyanate of silver is insoluble in cold water, but dissolves slightly in boiling water, and is precipitated therefrom as a powder on cooling. It dissolves readily in aqueous ammonia. (Wöhler.)

Ammonio-cyanate of Silver.—The solution of cyanate of silver in ammonia yields, on evaporation, large translucent laminæ, which give off their ammonia, and become opaque, both in air and in water. (Wöhler, *Gilb.* 73, 166; *Pogg.* 1, 120.)

Cyanate of baryta forms a brownish yellow precipitate with chloride of gold. (Wöhler.)

Hydrosulphocyanic Acid. C^2NHS^2.

Literature for Hydrosulphocyanic acid and the Sulphocyanides.

PORRETT. *Phil. Trans.* 1814, 527; also *Schw.* 17, 258; also *Gilb.* 53, 184. *Ann. Phil.* 13, 356.
GROTTHUSS. *Schw.* 20, 225; 32, 272.
A. VÖGEL. *Schw.* 23, 15.
WÖHLER. *Gilb.* 69, 271.
BERZELIUS. *Schw.* 31, 42.
LIEBIG. *Pogg.* 15, 548. *Ann. Pharm.* 10, 9; also *Pogg.* 34, 576. *Ann. Pharm.* 26, 174; 39, 199; 50, 337; 53, 330.
PARNELL. *Phil. Mag. J.* 17, 249; also *Ann. Pharm.* 39, 198.
VÖLCKEL. *Ann. Pharm.* 43, 80. *Pogg.* 58, 135; 61, 353; 62, 106 and 607; 63, 106; 65, 312.
CLAUS. Sulphocyanides. *J. pr. Chem.* 15, 401.
MEIZENDORFF. Sulphocyanides. *Pogg.* 56, 63.

Schwefelblausäure, Blutsäure, Andrazothionsäure (Grotthus), *Sulphuretted Chyazic acid* (Porrett), *Rhodanwasserstoffsäure* (Berzelius), *Schwefelcyanwasserstoffsäure, Acide sulfocyanhydrique.*

Hydrosulphocyanic acid was first observed by Bucholz (*Beitr. zur Erweiterung u. Berichtigung der Chemie,* 1799, 1, 88), and by Rink (1804), (*A. Gehl,* 2, 460), afterwards more distinctly recognized by Porrett (1808), determined as to its quantitative constitution by Berzelius, and further examined by Liebig, Völckel, and others.

In accordance with the radical-theory, hydrosulphocyanic acid is generally expressed by the formula H,C^2NS^2, and regarded as the

hydrogen-acid of a hypothetical called *Sulphocyanogen* or *Rhodanogen* $=C^2NS^2$. In like manner, the compounds in which 1 At. hydrogen is replaced by 1 At. of a metal, *e.g.*, C^2NK,S^2, are regarded as compounds of the metals with sulphocyanogen, *e. g.*, K,C^2NS^2, and called *Sulphocyanides* or *Rhodanides*. As these terms have been actually introduced and gained acceptance, they will be used in the present work, although the theory on which they are based is different from that to which the preference is here given. According to the latter theory, hydrosulphocyanic acid and sulphocyanide of potassium are respectively C^2NH,S^2 and C^2NK,S^2, that is to say, compounds of the nucleus C^2NH (hydrocyanic acid), and C^2NK (cyanide of potassium), with 2 At. sulphur, precisely analogous to cyanic acid C^2NH,O^2, and cyanate of potash C^2NK,O^2, excepting that, in this case, 2 At. oxygen are placed outside the nucleus, instead of 2 At. sulphur. If, in accordance with the radical-theory, we write cyanic acid: C^2NO,HO, we may then express hydrosulphocyanic acid and sulphocyanide of potassium by the formulæ C^2NS,HS and C^2NS,KS, adopted by Völckel, who likewise regards hydrosulphocyanic acid as cyanic acid, in which the oxygen is replaced by sulphur.

H. Davy (*Gilb.* 54, 384) observes, indeed, that sulphocyanogen is formed when cyanide of mercury is heated with sulphur; and Kemp remarks that liquid cyanogen under strong pressure is converted by sulphur into a dark grey substance, which, after the excess of cyanogen has been suffered to escape by opening the tube, is found to be a compound of sulphur and cyanogen; but neither of these chemists has further examined whether sulphocyanogen (C^2NS^2) is actually formed in this case. That the yellow powder separated from sulphocyanide of potassium by the action of chlorine or nitric acid is not really sulphocyanogen, as it was first supposed to be, is now universally admitted; hence we must conclude that sulphocyanogen in the free state has not yet been obtained.

Sources. Sulphocyanide of potassium or sodium occurs in the saliva of man and of the sheep. (Gm.) Göbel found it in a human salivary calculus. The reddening of ferric salts by human saliva was first observed by Previranus, and Gmelin merely found in addition that the effect was due to hydrosulphocyanic acid. Every specimen of human saliva which the author examined, produced this reddening of a solution of sesquichloride of iron; and if other chemists have failed to obtain it, the failure probably arises from a too sparing use of the iron-salt, the ferric oxide being in consequence completely precipitated by the alkali of the saliva. Ure (*N. Quart. J. of Sc.* 7, 60; also *N. Br. Arch.* 37, 101) likewise demonstrated, in the most distinct manner, the presence of hydrosulphocyanic acid in human saliva.

Formation of Hydrosulphocyanic acid and the Sulphocyanides.—1. Sulphocyanide of potassium is formed when cyanide or ferrocyanide of potassium is gently ignited with sulphur, or when aqueous cyanide of potassium is boiled with sulphur, or when nitrogenous charcoal is ignited with carbonate of potash and sulphur, or with sulphate of potash. (Porrett).—2. Cyanogen gas is absorbed by heated bisulphide of potassium, converting it into sulphocyanide. Pentasulphide of potassium forms the same compound, with evolution of 3 At. sulphur. So likewise in the wet way, 3 At. sulphur being precipitated:

$$C^2N + KS^2 = C^2NKS^2;\ C^2N + KS^5 = C^2NKS^2 + S^3.$$

but if protosulphide of potassium be used, no sulphur is precipitated, and cyanide of potassium is formed as well as sulphocyanide:

$$2C^2N + 2KS = C^2NK + C^2NKS^2;$$

if sulphide of hydrogen and potassium be used, bi-hydrosulphate of cyanogen is likewise formed. (Wöhler, *Pogg.* 3, 181.)—It had been previously observed by Gay-Lussac, that cyanogen gas is absorbed by heated sulphide of barium without separation of sulphur, and a brown mass formed, the colourless aqueous solution of which imparts a brown colour to ferric salts. — 3. The aqueous solution of cyanide of mercury is decomposed by tersulphide of potassium, yielding sulphocyanide of potassium, and sulphide of mercury (Porrett):

$$HgCy + KS^3 = KCyS^2 + HgS.$$

A similar reaction is produced when prussian blue is boiled, for a long time, with the aqueous solution of potash liver of sulphur. (Porrett.)—4. Hydrosulphocyanic acid is evolved when sulphur is heated with prussian blue. (A. Vögel.) — 5. Hydrocyanic acid, with sulphur and aqueous ammonia, to which a certain quantity of hydrosulphate of ammonia has been added, forms hydrosulphocyanate of ammonia. (Liebig, *Ann. Pharm.* 61, 126):

$$C^2NH + NH^3 + 2S = NH^3,C^2NHS^2.$$

In this reaction, the sulphide of ammonium acts merely as a carrier of the sulphur, dissolving it and forming a polysulphide of ammonium, and then giving it up again to the hydrocyanate of ammonia, whereby the latter is converted into hydrosulphocyanate. Sulphocyanide of potassium is likewise formed on mixing the aqueous solution of pentasulphide of potassium with hydrocyanic acid, hydrosulphuric acid being at the same time evolved, and sulphur precipitated (Gm.):

$$C^2NH + KS^5 = C^2NKS^2 + HS + S^2.$$

6. Aqueous hydrocyanic acid, saturated with hydrosulphuric acid, is converted, on exposure to the air, into hydrosulphocyanic acid, in proportion as the hydrogen of the hydrosulphuric acid is taken up by the oxygen of the air. Hence the contamination of Vauquelin's prussic acid (VII. 393), with hydrosulphocyanic acid. According to Pelouze (*Ann. Chim. Phys.* 44, 218), an aqueous mixture of hydrocyanic acid, sulphuretted hydrogen, and sesquichloride of iron yields hydrosulphate of ferrous oxide on exposure to the air.—7. Hydrosulphocyanate of ammonia is formed in the decomposition of sulphide of carbon by aqueous or alcoholic ammonia. (Zeise, II. 205.)—8. When animal substances are charred by heating with oil of vitriol, the residue, on being subjected to a stronger heat, yields, among other products, hydrosulphocyanate of ammonia. (O. Henry, *J. Chim. méd.* 21, 301.)—9. Hydrosulphocyanic acid is formed in certain decompositions of volatile oil of mustard.

Preparation and Properties.—When dry disulphocyanide of mercury is decomposed by passing hydrosulphuric or hydrochloric acid gas over it, hydrosulphocyanic acid collects in the tube as a colourless, oily liquid, which, in the cold, appears to crystallize in a radiated mass, but is quickly resolved into hydrocyanic acid vapour and hydro-persulphocyanic acid. (Wöhler.)

			Berzelius.	Grotthuss.
2 C	12	20·34	20·30	8·5
N	14	23·73	23·85	19·7
H	1	1·69	1·68	4·5
2 S	32	54·24	54·17	67·3
C^2NH,S^2	59	100·00	100·00	100·0

According to Porrett, it is composed of 34·8 p. c. (1 At.), hydrocyanic acid, with 65·2 p. c. (4 At.) sulphur.

Compounds.—A. With water. *Aqueous Hydrosulphocyanic acid.*

Preparation—1. By distilling sulphocyanide of potassium with dilute sulphuric, phosphoric, oxalic, or tartaric acid, not in excess.—Calculation gives, for 97·2 pts. (1 At.) sulphocyanide of potassium, 49 pts. (1 At.) of oil of vitriol, 63 pts. (½ At.) crystallized oxalic acid, or 75 pts. (½ At.) crystallized tartaric acid.—A. Vogel recommends for 100 pts. sulphocyanide of potassium dissolved in 100 pts. of water, 75 pts. of oil of vitriol, or, better, of phosphoric acid, diluted with 75 pts. water. According to this chemist, when sulphuric acid is used, sulphur (hydropersulphocyanic acid) and pentasulphide of ammonium pass over towards the end of the distillation, and the residue contains sulphur (hydropersulphocyanic acid), together with sulphate of potash, the quantity of sulphur being greater, as the sulphuric acid is more concentrated and used in greater excess. Whether the acid used be sulphuric, phosphoric, hydrochloric, or oxalic, partial decomposition always takes place, and the hydrosulphocyanic acid becomes consequently contaminated with hydrocyanic acid, sulphuretted hydrogen, and ammonia. (Liebig, *Pogg.* 34, 176).—If the liquid be sufficiently diluted, and the sulphuric acid be not used in excess, the product which it yields is as pure as that obtained with phosphoric acid. (Völckel.)—The amount of product is the same whether the sulphocyanide of potassium be distilled with sulphuric, phosphoric, or tartaric acid; but in consequence of partial decomposition, the quantity of hydrosulphocyanic acid obtained is never more than half that which might be expected from the quantity of sulphocyanide used. The decomposition-products are likewise the same, viz., in the residue an ammoniacal salt and hydropersulphocyanic acid, and in the distillate, hydrocyanic acid, sulphuretted hydrogen (even when the sulphocyanide of potassium is free from sulphide), and sulphide of carbon. The excess of sulphuretted hydrogen prevents the appearance of sulphurous acid in the distillate, but the liquid is often clouded by precipitated sulphur. These decomposition-products form in greater abundance, as the acid is more concentrated and in larger excess, and as the heat applied to distil the liquid is greater; in the contrary case, the formation of bisulphide of carbon does not take place. To avoid, however, too great dilution of the product, 97 parts of sulphocyanide of potassium may be distilled with 49 pts. of oil of vitriol, diluted with 196 pts. of water. If the distillate, which has a density of 1·0082, be exposed to the air for a few days, in a vessel covered with paper, it will give off the hydrocyanic and hydrosulphuric acids.

2. Sulphocyanide of silver or disulphocyanide of mercury, obtained by precipitating nitrate of silver or mercurous nitrate with sulphocyanide of potassium, is washed, suspended in water, and decomposed by a stream of sulphuretted hydrogen gas; the liquid is then filtered, and the admixed sulphuretted hydrogen removed by careful evaporation, or by carefully

adding a portion of the reserved precipitate. (Berzelius.)—It is in this way only, and not by (1), that the acid can be obtained in a state of purity; the sulphocyanide of silver may also be decomposed by dilute hydrochloric acid instead of sulphuretted hydrogen. (Liebig.)—E. Böckmann (*Ann. Pharm.* 21, 155), decomposes sulphocyanide of lead by sulphuretted hydrogen in a similar manner; but, according to Völckel and Meitzendorff, this decomposition is slow and incomplete.

3. Sulphocyanide of barium is decomposed by an exactly equivalent quantity of dilute sulphuric acid. (Berzelius, *Lehrb.*)

Colourless liquid, whose greatest density is 1·022. (Porrett.) Freezes at 12·5° in six-sided prisms, boils at 102·5°. (A. Vogel.) Boils at 85° (Artus, *J. pr. Chem.* 8, 253.) Has a pungent odour like that of strong acetic acid, reddens litmus strongly; tastes very sour; exerts a poisonous action like that of hydrocyanic acid; colours ferric salts blood-red, and, for that reason, reddens paper. (Porrett, A. Vogel.)

Decompositions. The dilute acid may be preserved both in open and in closed vessels; but when evaporated in the air, it turns yellow, and deposits a yellow powder [hydropersulphocyanic acid], which evolves ammonia when treated with potash. The aqueous acid also deposits a yellow powder when exposed to sunshine. Passed in the state of vapour through a red-hot tube, it is partly decomposed, without deposition of charcoal, into sulphur, hydrocyanic acid, and a small quantity of ammonia; if the tube contains iron, the products are hydrocyanic acid, sulphuretted hydrogen, and sulphide of iron. (A. Vogel.)—At each distillation, the hydrosulphocyanic acid leaves behind a certain quantity of sulphur [hydropersulphocyanic acid]. (Porrett.)—The aqueous acid decomposes when boiled—a portion, however, going off undecomposed, together with a large quantity of water—into carbonic acid, sulphide of carbon, sulphuretted hydrogen, and ammonia, and afterwards, when the residue has become more concentrated, into hydrocyanic and hydropersulphocyanic acids. (Völckel.) In this case there are three modes of decomposition to be considered (Völckel), viz.:

$$C^2NHS^2 + 2\,HO = CO^2 + CS^2 + NH^3.$$

further:

$$C^2NHS^2 + 4HO = 2CO^2 + 2HS + NH^3.$$

lastly:

$$3C^2NHS^2 = C^2NH + 2C^2NHS^3.$$

Hence, when sulphocyanide of potassium is distilled with dilute sulphuric acid, the only decomposition-products which pass over at first are hydrosulphuric acid and sulphide of carbon, hydrocyanic acid not appearing till towards the end of the process, and an ammoniacal salt remaining behind. (Völckel, *Ann. Pharm.* 43, 80; *Pogg.* 58, 135.)—2. When aqueous hydrosulphocyanic acid is boiled with a *stronger acid*, the same decomposition is produced as when it is boiled alone. Thus, on boiling it with hydrochloric or sulphuric acid, the products obtained are carbonic acid, sulphide of carbon, sulphuretted hydrogen, and ammonia, together with hydrocyanic and hydropersulphocyanic acids; the sulphuric acid may also yield sulphurous acid. (Völckel.)—Oil of vitriol, added to the aqueous acid, throws down sulphur [hydropersulphocyanic acid] (A. Vogel), carbonic acid, sulphurous acid, and ammonia being produced at the same time. (Grotthus.)—3. From concentrated hydrosulphocyanic acid, *chlorine* precipitates pseudosulphocyanogen; the more dilute acid is

completely decomposed by it, yielding cyanogen [chloride of cyanogen?] sulphuric acid, and hydrochloric acid (Völckel, *Ann. Pharm.* 43, 93; *Pogg.* 58, 145):

$$4C^2NHS^2 + HO + 3Cl = C^8N^4H^2S^8O + 3HCl;$$

and:

$$C^2NHS^2 + 6HO + 7Cl = C^2N + 2SO^3 + 7HCl.$$

Hence Grotthuss, who probably used a rather strong acid, obtained a yellow precipitate with chlorine, and A. Vogel, probably from using a more dilute acid, obtained no precipitate, but a mixture of hydrocyanic acid, sulphuric and hydrochloric acids. — 4. *Iodine*, heated with the aqueous acid, forms no sulphuric acid, but only hydriodic acid, hydrocyanic acid which escapes, and iodide of sulphur which is precipitated. (A. Vogel.) — 5. *Iodic acid* decomposes hydrosulphocyanic acid. (L. Thompson.) — 6. A mixture of *chlorate* of potash and hydrochloric acid yields hydrocyanic and sulphuric acid (Porrett); according to Grotthuss, however, it yields no hydrocyanic acid, but sulphuric acid, carbonic acid, and ammonia.—7. Hot *nitric* acid produces sulphuric acid (Porrett), with evolution of carbonic and hydrocyanic acid. (A. Vogel.) (Laurent & Gerhardt, *N. Ann. Chim. Phys.* 19, 100), who regard pseudosulphocyanogen as $C^6N^3HS^6$, assume the following equation:

$$3C^2NHS^2 + NO^5 = NO^3 + 2HO + C^6N^3HS^6.$$

8. Aqueous hydrosulphocyanic acid, saturated with *sulphuretted hydrogen*, and set aside in a closed vessel, is decomposed into sulphide of carbon and ammonia (Völckel, *Pogg.* 65, 312):

$$C^2NHS^2 + 2HS = C^2S^4 + NH^3.$$

9. In contact with zinc, hydrosulphocyanic acid evolves sulphuretted hydrogen. (Percy, *Repert.* 81, 108.) This effect takes place very rapidly and abundantly even at ordinary temperatures; iron acts much more slowly. (Gm.)

Sulphocyanides.

These compounds are formed by the processes mentioned on pages 71, 72,—also by bringing aqueous hydrosulphocyanic acid in contact with a metallic oxide, and by double decomposition.

Most, if not all sulphocyanides are resolved, either at a low or at a high red heat, into nitrogen, cyanogen, sulphide of carbon, and a metallic sulphide (Wöhler, Meitzendorff, Völckel):

$$4C^2NMS^2 = N + 3C^2N + 2CS^2 + 4MS.$$

We may suppose that, at the beginning of the decomposition, sulphide of carbon is given off, and a mixture of metallic sulphide and mellon (supposed $= C^6N^4$) remains; and that this, when the heat is continued, is resolved into cyanogen and nitrogen gases:

$$4C^2NMS^2 = 2CS^2 + 4MS + C^6N^4.$$

Völckel (*Pogg.* 63, 106), states, that the residual sulphide is mixed with a small quantity of a yellow powder resembling mellon, but only when the sulphocyanide is not quite anhydrous,—for the yellow powder contains from 1 to 2 per cent. of hydrogen. According to Meitzendorff and Völckel, also, the evolution of cyanogen and nitrogen gases goes on from

the very beginning of the decomposition.—Sulphocyanides heated with hydrate of potash, give off carbonate of ammonia. (Claus, *J. pr. Chem.* 15, 410.)—The stronger acids, in a state of dilution, separate hydrosulphocyanic acid (distinguished by its pungent acid smell), at ordinary temperatures, only from those sulphocyanides, whose metals form sulphides decomposible by acids,—consequently, not from the sulphocyanides of copper, mercury, and silver. (Völckel.)—The sulphocyanides of mercury and silver, when suspended in water, are decomposed by sulphuretted hydrogen, yielding metallic sulphides and aqueous hydrosulphocyanic acid; but the sulphocyanides of copper, lead, and most of the other heavy metals, either resist the action of sulphuretted hydrogen, or are but very imperfectly decomposed by it. (Völckel.) In this reaction, it may be supposed that the sulphocyanide of silver, for example, gives up its 1 At. silver to the sulphur of the HS, the hydrogen of which takes the place of the silver. — Several other decompositions of sulphocyanides will be given in speaking of sulphocyanide of potassium.

Most sulphocyanides are soluble in water. The solutions may be supposed to contain hydrosulphocyanates of metallic oxides:

$$KCyS^2 + HO = KO,HCyS^2.$$

Most sulphocyanides likewise dissolve in alcohol.—The soluble sulphocyanides form white precipitates insoluble in water, with a mixture of a cupric salt and sulphurous acid or green vitriol,—also with mercurous, silver, and auric salts. With ferric salts they produce a blood-red colour —or reddish yellow, in case of very great dilution—which is distinguished from other similar tints produced in ferric salts, by not changing to pale yellow on the addition of a large quantity of hydrochloric acid; moreover, according to Percy, the immersion of a piece of zinc in the mixture causes an evolution of sulphuretted hydrogen, which imparts a brown colour to paper moistened with acetate of lead and held over it.

Sulphocyanide of Ammonium, or *Hydrosulphocyanate of Ammonia*, $C^2N(NH^4),S^2 = NH^3,C^2NH,S^2 = NH^4,CyS^2$.

Preparation. 1. By neutralizing hydrosulphocyanic acid with caustic ammonia or carbonate of ammonia. (Porrett.) — 2. By saturating 2 pts. of aqueous ammonia of sp. gr., 0·95 with sulphuretted hydrogen; adding 6 pts. more of the same ammonia and 2 pts. of flowers of sulphur, together with the hydrocyanic acid obtained by distilling 6 pts. of ferrocyanide of potassium, 3 pts. oil of vitriol, and 18 pts. water; digesting the mixture over the water-bath till the liquid turns yellow, and ceases to take up sulphur; then boiling it till it becomes colourless, in consequence of the decomposition of the polysulphide of ammonium and precipitation of sulphur; and evaporating the filtrate to the crystallizing point. This process yields from $3\frac{1}{3}$ to $3\frac{1}{2}$ pts. of dry, snow-white salt. (Liebig, *Ann. Pharm.* 61, 126.) — 3. Disulphocyanide of copper is decomposed by digestion with protosulphide of ammonium, and the liquid filtered from the sulphide of copper. (Liebig. *Ann. Pharm.* 53, 330.) — 4. An aqueous solution of sulphocyanide of ammonium and sal-ammoniac is evaporated to dryness, the pulverized residue digested in alcohol, and the solution evaporated. The resulting salt is contaminated with small quantities of sulphocyanide of potassium and sal-ammoniac. (Völckel, *Pogg.* 61, 354.) Even if the hydrochlorate or sulphate of ammonia and the sulphocyanide of potassium be used in exactly equal numbers of atoms, the liquid obtained by digestion with alcohol contains

as much sulphocyanide of potassium as sulphocyanide of ammonium. (Liebig.)

On evaporating the concentrated aqueous solution over oil of vitriol, the salt is obtained in anhydrous, shining, somewhat deliquescent tables. (Meitzendorff); from absolute alcohol it crystallizes in large, transparent, colourless, non-deliquescent laminæ, which, at 145° (at 170°, according to Völckel), fuse to a colourless liquid. (Liebig.)

			Meitzendorff.
NH^3	17	22·37	21·94
C^2NHS^2	59	77·63	
NH^3,C^2NHS^2	76	100·00	

This salt is precisely analogous in composition to cyanate of ammonia and, therefore also, to urea, the O being replaced by S. (Liebig.)

The salt, which melts at 145°, begins to decompose at 160°, gradually assuming a brown colour, giving off sulphide of carbon, sulphuretted hydrogen, and ammonia, depositing a continually increasing quantity of a yellowish grey substance (transparent and crystalline under the microscope), and gradually solidifying again, at a higher temperature, in the form of yellow mellon, C^6N^4 (Liebig, *Ann. Pharm.* 53, 330):

$$4C^2N^2H^4S^2 = 2CS^2 + 4HS + 4NH^3 + C^6N^4.$$

If the heat be raised high enough, there remains a mixture which may be regarded as a compound of mellon with varying quantities of ammonia, *e. g.* as melam, $C^{12}N^{11}H^9$. But if access of air and moisture be entirely prevented, not a trace of hydropersulphocyanic acid or cyanide of ammonium passes over; no free sulphur sublimes; neither does sulphur remain in the residue. (Liebig.) If the sulphocyanide of ammonium be merely heated till it solidifies, and the residue be washed with cold water, the water continually acquires the property of colouring ferric salts blood-red. With cold dilute potash, the residue of the distillation forms soluble sulphocyanide of potassium and an insoluble body free from sulphur, which when exhausted with boiling water, yields a filtrate, which, on cooling, deposits a few white flakes (appearing under the microscope as a mixture of white flakes and needles). If the residue of the distillation be dissolved in hot potash-ley and the liquid evaporated, it is resolved into melam and ammelin. (Liebig.)—A perfectly dry mixture of 1 pt. sulphocyanide of potassium and 2 pts. sal-ammoniac behaves, when distilled, exactly like sulphocyanide of ammonium. The decomposition begins a few degrees above 100°, and is more complete as the heat is raised more slowly. In this case, also, nothing is evolved but sulphide of carbon, sulphuretted hydrogen, and ammonia; consequently, crystals of [bi]-hydrosulphate of ammonia sublime, and there remains, together with the chloride of potassium, a quantity of melam holding hydrochloric acid in a state of combination: $8C^2N^2H^4S^2 = 4CS^2 + 8HS + 5NH^3 + C^{12}H^{11}N^9$. No free ammonia passes over at any stage of the decomposition. [The opposite statement of Liebig previously given, is probably the more correct of the two, supposing that his equation is right; for at ordinary temperatures, monohydrosulphate of ammonia cannot exist in the solid state, so that the salt actually formed must be the bihydrosulphate; hence the 8HS are only sufficient to form $4NH^3$, whereas, according to the above equation, $5NH^3$ are set free.]—The yellow greyish white mass, when freed from chloride of potassium by washing with cold water, a process which takes a long time, leaves the compound of melam

with hydrochloric acid, which has abstracted the melam from a portion of the sal-ammoniac. (Liebig, *Ann. Pharm.* 10, 10; 53, 333.)

In the dry distillation of sulphocyanide of ammonium, sulphide of carbon, sulphuretted hydrogen, and ammonia, are gradually evolved; but the residue consists of Völckel's *Poliene*, $C^6N^6H^6$, the decomposition taking place as shown in the following equation:

$$4C^2N^2H^4S^2 = 2CS^2 + 4HS + 2NH^3 + C^6N^6H^6.$$

(Laurent & Gerhardt, *N. Ann. Chim. Phys.* 19, 97; *comp.* Gerhardt, *Compt. rend.* 18, 159; also *J. pr. Chem.* 31, 438).

Sulphocyanide of ammonium begins to decompose at 205°, boiling slightly, and giving off, first ammonia, then sulphide of carbon, and the products to be named hereafter; but at 205° the decomposition stops after awhile almost entirely. If the heat be then raised a few degrees higher, the decomposition begins again; but even when it is gradually raised to 250°, the residue still remains liquid, but, nevertheless, exhibits a darker colour. If the heat be then maintained between 260° and 270°, till the evolution of gas, which is violent at first, begins to slacken, certain volatile products are found to have been evolved in the following order, reckoning from the beginning of the heating: Ammonia, then sulphide of carbon, polysulphide of ammonium, hydrosulphocarbonate of ammonia (in yellow feathery crystals), hydrocyanate of ammonia, and hydrosulphocyanate of ammonia. The residue, which solidifies on cooling, contains: Undecomposed hydrosulphocyanate of ammonia, which may be dissolved out by water; a yellow body deposited, on cooling, from the boiling aqueous extract; sulphide of *Alphene*, $C^{10}N^{10}H^{10}S^2$; a small quantity of sulphide of *Phelene*, $C^{12}N^{12}H^{12}S^2$, and a red crystalline substance (these three dissolved out by hot water); and a small quantity of a brownish substance, together with sulphur (these two remain after the residue has been boiled with water).—Hence, hydrosulphocyanate of ammonia, when heated, first gives off a portion of its ammonia; then the greater part of the hydrosulphocyanic acid is resolved into hydropersulphocyanic and hydrocyanic acid, the latter volatilizing with the ammonia, while the hydropersulphocyanic acid undergoes various decompositions, whereby with addition of the remaining ammonia, the above-named products are formed. (Völckel.) When hydrosulphocyanate of ammonia is heated to 300°, the same decomposition-products are evolved as at 250°; but the residue becomes more viscid and contains hydrosulphocyanate of ammonia which may be dissolved out by cold water, sulphide of phelene and sulphide of *Argene*, $C^{16}N^{16}H^{16}S^2$, extractable by hot water, and a residue consisting of *Poliene*, $C^6N^6H^6$, mixed with small quantities of other products. By continued exposure to a heat between 310° and 320°, hydrosulphocyanate of ammonia is almost wholly decomposed, the same volatile products being evolved; the residue in this case becomes gradually pasty, then solid, and consists almost entirely of poliene, with a small quantity of the fixed products formed at 300°. (Völckel, *Pogg.* 61, 353; 63, 106; 65, 312.) [Whether the several sulphides distinguished by Völckel are really peculiar compounds, and not, for the most part, mere mixtures, is a question which remains to be decided.]

Hydrosulphocyanate of ammonia is deliquescent, and dissolves readily in water and alcohol.

Sulphocyanide of Potassium.—*Preparation.* 1. An intimate mixture of 2 pts. ferrocyanide of potassium and 1 pt. sulphur, is gently heated

in a glass or a covered crucible, stirring all the while with an iron rod, and keeping the temperature considerably below redness—which is best ensured by heating in a sand-bath—till the mass comes into a state of tranquil fusion and throws up no more bubbles, and till a sample, dissolved in water and added to a dilute solution of a ferric salt, no longer yields prussian blue, but a blood-red colouring. The cooled black mass is pulverized and exhausted with water. The solution, which is colourless at first, acquires a red tint by exposure to the air or to fumes of nitrous acid, inasmuch as it contains ferrous sulphate, which, by oxidation, is converted into ferric sulphate. The ferrous oxide is precipitated hot by pure potash or its carbonate, and evaporated to the crystallizing point. (Grotthuss, A. Vogel.) For the theory of this process, *vid.* VII, 459, 460. If the fusion be not continued long enough, a portion of the ferrocyanide remains undecomposed; if it be too long continued, the sulphocyanide of iron—which is formed together with the sulphocyanide of potassium, and is yet to be converted into the latter—becomes decomposed; and, moreover, its decomposition is attended with the formation of mellon, which converts part of the sulphocyanide of potassium into mellonide. In that case, also, access of air to the over-heated mass may give rise to the formation of carbonate, and, according to Völckel, also of cyanate of potash.—It is useful to evaporate the liquid filtered from the precipitated ferrous oxide to a small bulk, and dissolve it in warm alcohol of 36° Bm. This leaves ferrocyanide of potassium, carbonate of potash (proceeding from the precipitation of the iron), and other impurities undissolved; and the filtrate set aside for some time in the cold, frequently deposits mellonide of potassium, whereupon the liquid must be filtered, distilled, and evaporated to the crystallizing point. (Gm.) Since carbonate of potash is slightly soluble in alcohol, it is best not to precipitate the iron completely by carbonate of potash, but to throw down the last portions by hydrosulphate of ammonia, which may then, after filtration, be separated by evaporation and fusion. (Liebig, *Pogg.* 15, 553.) To save the purification by alcohol, Meillet (*J. Pharm.* 27, 628), neutralises with acetic acid the liquid filtered from the precipitated ferrous oxide, in case it be alkaline—evaporates—and purifies the crystals of sulphocyanide of potassium by evaporation. From the mother-liquid containing the acetate of potash he obtains sulphocyanide of lead by precipitating with acetate of lead.—Turner's method (*Edinb. J. of Sc.* 5, 248) of heating the mixture, with agitation, in an open porcelain dish, till the escaping sulphide of carbon ceases to burn with flame, is rather disadvantageous than otherwise. — 2. A mixture of 46 pts. (1 At.) of roasted ferrocyanide of potassium, 17 pts. (nearly 1 At.) of carbonate of potash, and 32 pts. (8 At.) of sulphur, is heated till it attains a state of clear and tranquil fusion; then raised to a low red heat to decompose the hyposulphite of potash formed at the commencement of the process; afterwards left to cool, boiled with alcohol, and filtered. On the filter there remains bisulphide of iron in fine scales and sulphate of potash (neither carbonate of potash nor mellonide of potassium); the transparent and colourless filtrate yields crystals of pure sulphocyanide of potassium. (Liebig. *Ann. Pharm.* 50, 345; 51, 288.) [An advantageous process.]—¶ Henneberg (*Ann. Pharm.* 73, 228) modifies the latter part of the process so far as to boil the fused mass repeatedly with water, separate the liquid from the sulphide of iron by decantation, neutralize it, if necessary, with sulphuric acid, evaporate to the crystallizing point, and purify the resulting salt by recrystallization from alcohol. ¶ — 3. An aqueous solu-

tion of 65·2 pts. (1 At.) cyanide of potassium is digested with 32 pts. (2 At.) finely pounded sulphur, till the sulphur dissolves. If a larger quantity of sulphur be used, the solution turns yellowish, from formation of a polysulphide of potassium. (Wiggers, *Ann. Pharm.* 29, 319.) 4. Aqueous cyanide of mercury is decomposed by an exactly equivalent quantity of tersulphide of potassium, and the liquid filtered. (Duflos, *Schw.* 65, 237):

$$HgCy + KS^3 = HgS + KCyS^2.$$

5. A mixture of 30 pts. cyanide of mercury, 12 pts. hydrate of potash, and 14 pts. sulphur is heated till it attains a state of tranquil fusion; the blackish grey mass pulverized and treated while yet warm with absolute alcohol; and the solution separated by filtration from the sulphide of mercury (to which a trace of running mercury adheres). (Artus, *J. pr. Chem.* 8, 252). The sulphocyanide of potassium crystallized from the filtrate, is less deliquescent than the same salt obtained in other ways. (Artus, Böttger, *J. pr. Chem*: 10, 64.)—Porrett boiled 3 or 4 parts of prussian blue with the aqueous solution of 1 pt. potash liver of sulphur; acidulated the filtrate slightly with sulphuric acid; heated it for a while; then left it to stand in the cold in contact with powdered black oxide of manganese, to decompose the sulphide of potassium and hyposulphite of potash; precipitated sulphocyanide of copper from the filtrate, by adding a mixed solution of 2 pts. sulphate of copper and 3 pts. green vitriol; and decomposed the precipitate, after washing, with aqueous potash.

Properties. Long, transparent, colourless, striated prisms and needles with 4-sided summits; at a temperature considerably below redness, they fuse to a transparent and colourless liquid, which solidifies in a crystalline mass on cooling. (Grotthuss.) Tastes like horse-radish at first, saline and cooling afterwards. (Grotthuss.) Tastes saline and cooling like nitre (Berzelius). A narcotic poison, like hydrocyanic acid. (A. Vogel.)

According to Berzelius.

2 C	12·0		12·35
N	14·0		14·40
K	39·2		40·33
2 S	32·0		32·92
C^2NK,S^2	97·2		100·00

Decompositions. 1. Sulphocyanide of potassium, when kept from contact with the air, sustains a moderate red heat without decomposition, and does not form mellonide of potassium; when ignited in the air, however, it burns and forms sulphate of potash; and when heated in moist air or in the moist state, it gives off carbonic acid and carbonate of ammonia, while sulphide of potassium remains mixed with the residue. (Berzelius.) A mixture of this salt with 5 parts chlorate of potash detonates violently, either by percussion or when touched with oil of vitriol. The light which accompanies this deflagration is purple-red. (Johnston, *Schw.* 57, 379.)—2. Aqueous sulphocyanide of potassium, even when kept in closed bottles, suffers gradual decomposition, attended with formation of ammonia; at a boiling heat it decomposes more quickly. (A. Vogel.) The solution may be rendered more stable by mixing it with alcohol.

3. When *chlorine gas* is passed over sulphocyanide of potassium in a state of fusion, the salt froths up violently and becomes yellow and

opaque, continually increasing in viscidity, and finally solidifying. In this reaction, chloride of sulphur volatilizes, and likewise fixed chloride of cyanogen, the latter subliming in needles, and amounting to 4 or 5 per cent. of the sulphocyanide of potassium; at a certain stage of the decomposition there arises a thick red vapour, which forms a red and yellowish red, laminar sublimate. The residue is a mixture of chloride of potassium and impure mellon. (Liebig.) — If the sulphocyanide of potassium be not heated above its melting point, the chloride of sulphur which passes over at the beginning is accompanied by another product; then follows the chloride of cyanogen.—The red and yellowish red sublimate, freed from adhering chloride of cyanogen by heating in the air, contains 67·9 per cent. of sulphur, and appears as a compound analogous to pseudosulphocyanogen, but richer in sulphur. When gently heated in dry chlorine gas, it gives up chloride of sulphur, and is converted into a reddish yellow compound, which retains only 57·05 per cent. of sulphur. This compound is insoluble in aqueous potash, but partially soluble in water after the potash has been poured off. — If the chloride of potassium be dissolved out of the residue by water, there remains a light powder of a bright yellow colour, which is wholly or nearly free from sulphur, dissolves in alkalis and in nitric acid, is converted into cyanylic acid by long boiling with the latter, and, after ignition, exhibits all the characters of mellon. (Liebig, *Pogg.* 15, 548; *Ann. Pharm.* 10, 6, and 38; 43, 97.)

If the chlorine gas used has been first completely freed from hydrochloric acid by passing it through water and then over chloride of lime, and afterwards dehydrated by chloride of calcium, almost the only products obtained are chloride of sulphur, chloride of cyanogen, and chloride of potassium, with little or no yellowish red sublimate or mellon, the formation of which is probably due to the water remaining in the sulphocyanide of potassium, even after long fusion. (Völckel. *Ann. Pharm.* 43, 97; *Pogg.* 50, 152.) — Chlorine gas passed through aqueous sulphocyanide of potassium throws down pseudosulphocyanogen, of an orange-yellow colour, but inclining more to red as the solution is stronger; very weak solutions yield no precipitate. The liquid soon becomes very acid, and is decomposed by excess of chlorine, yielding sulphuric, carbonic, and hydrochloric acids, also ammonia, if the excess of chlorine be not too great. (Liebig, *Pogg.* 15, 548; *Ann. Pharm.* 39, 212; 50, 337.) If the concentrated solution of sulphocyanide of potassium be kept cold while the chlorine is passed through it, sulphuric acid and hydrocyanic acid, or cyanogen, are produced, as well as the orange-yellow precipitate; but ammonia and carbonic acid are formed only when the sulphocyanide of potassium contains cyanate of potash. On evaporating the filtrate, hydrochloric acid is evolved, and there remains a small quantity of sulphate of potash, together with a large quantity of chloride of potassium. The chlorine at first produces the following decomposition:

$$C^2NKS^2 + 7Cl + 6HO = KCl + 2SO^3 + 6HCl + C^2N.$$

Afterwards the 8 At. acid thus formed act upon 8 other At. sulphocyanide of potassium, and the whole process is then as follows (Völckel):

$$9C^2NKS^2 + 13Cl + 10HO = 2(KO,SO^3) + 7KCl + 6HCl + C^2N + 2C^8N^4S^8H^2O$$

When chlorine gas is passed through a solution of sulphocyanide of potassium, sulphuric and cyanic acid are formed at the very beginning of

the action. If pseudosulphocyanogen be regarded as $C^{12}N^6H^3S^{12}O$, the equation is:

$$6C^2NKS^2 + 6Cl + 3HO = C^{12}N^6H^3S^{12}O + 6KCl + 2O.$$

The 2 At. O thus set free give rise to the formation of sulphuric and cyanic acid. From a dilute solution, chlorine throws down pale yellow hydrothiocyanic acid, instead of pseudosulphocyanogen. (Parnell, *Phil. Mag. J.* 17, 249; also *Ann. Pharm.* 39, 198.) — If cyanic acid were produced in the decomposition by chlorine, it would be decomposed into carbonic acid and ammonia; but neither of these compounds is actually present; moreover, Parnell's equation does not explain the formation of free hydrochloric acid.

When chlorine gas is passed through a concentrated solution of sulphocyanide of potassium, the containing vessel not being artificially cooled, the liquid soon becomes heated to the boiling point, gives off undecomposed hydrosulphocyanic acid, together with carbonic acid, and a small quantity of cyanogen, and yields a yellow precipitate, while hydrochloric acid, sal-ammoniac, and acid sulphate of potash remain in solution. The precipitate has a paler yellow colour than pseudosulphocyanogen, contains 18·22 p. c. C, 1·26 H, and 55·86 S, and is probably, therefore, $C^8N^4H^3S^9O$; it dissolves very sparingly in boiling alcohol, forming a solution which precipitates lead and silver-salts yellow. (Völckel.) — To explain the formation of pseudosulphocyanogen from sulphocyanide of potassium, Laurent & Gerhardt (*N. Ann. Chim. Phys.* 19, 100), who assign to pseudosulphocyanogen the formula $C^6N^3HS^6$, give the following equation:

$$3C^2NHS^2 + 2Cl = 2HCl + C^6N^3HS^6.$$

It is not, however, the decomposition of hydrosulphocyanic acid, but that of sulphocyanide by chlorine that we require to explain; for the latter we obtain the improbable equation:

$$3C^2NKS^2 + 2Cl + HO = 2KCl + KO + C^6N^3HS^6.$$

According to this view, the liquid should be rendered alkaline by the KO; but in reality it becomes very acid, and that too *from the very beginning*.

A. Vogel, in passing chlorine through an aqueous solution of sulphocyanide of potassium (probably very dilute), obtained no precipitate, the whole of the sulphur being converted into sulphuric acid.

4. Strong *nitric acid*, added to an aqueous solution of sulphocyanide of potassium, likewise throws down pseudosulphocyanogen.—On mixing from 2 to 2½ pts. of nitric acid of sp. gr. 1·43 with the cold solution of 1 pt. sulphocyanide of potassium in 3 pts. water, decanting the mixture from the crystals of nitre thereby produced, and heating it gently, it suddenly begins to boil spontaneously, effervescing violently, from escape of nitric oxide and carbonic acid, and yielding a precipitate of pseudosulphocyanogen. (Liebig, *Pogg.* 15, 548.) — Völckel also (*Ann. Pharm.* 43, 95) obtained, on heating the mixture, nitric oxide, carbonic acid, sulphuric acid, ammonia, and a yellow precipitate. As this precipitate contains 18·85 p. c. C, 1·25 H, and 54·11 S, Völckel regards it as a mixture of pseudosulphocyanogen and hydropersulphocyanic acid, supposing that of the hydrosulphocyanic acid set free by the nitric acid, one portion is resolved into hydrocyanic and hydropersulphocyanic acid; a second being partially oxidated by the nitric acid, yields pseudosulpho-

cyanogen; while a third is converted, by complete oxidation, into carbonic acid, sulphuric acid, and ammonia.—If the pseudosulphocyanogen be regarded as $C^{12}N^6H^3S^{12}O$, it will be formed by the oxygen of the nitric acid, according to the following equation (Parnell):

$$6C^2NKS^2 + 3HO + 6NO^5 + 4O \text{ (from the excess of nitric acid)} = C^{12}N^6H^3S^{12}O + 6(KO,NO^5).$$

5. Dry *hydrochloric acid* gas passed over melted sulphocyanide of potassium decomposes it very violently, with evolution of hydrocyanic acid, sulphide of carbon, and sal-ammoniac, and sublimation of a thick yellowish red mass. This red sublimate, when exposed to damp air, gives off acid vapours which redden ferric salts. It dissolves sparingly in cold, more abundantly in boiling water. The reddish yellow solution reddens litmus strongly, and reddens ferric salts in the same manner as hydrosulphocyanic acid. As long as it is maintained at a boiling heat, it gives off vapour of sulphide of carbon with effervescence, even if the red sublimate had been heated before it was dissolved in water. The aqueous solution, when cooled, deposits a reddish yellow powder, which contains a large quantity of sulphur, is neutral to litmus after washing, dissolves very readily in hot water, and may be separated from that solution in its original state. The solution forms, with nitrate of silver, thick yellow flakes, which, when heated in the liquid, give off a gas, and become black or blackish green. The red sublimate dissolves completely in alcohol, forming a red liquid, which smells like garlic and does not redden litmus. (Liebig, *Pogg.* 34, 576.)—When hydrochloric acid gas is passed through a saturated aqueous solution of sulphocyanide of potassium, the liquid being kept constantly cool, hydropersulphocyanic acid is precipitated, while sulphide of carbon and carbonic acid are formed in the solution—small, however, in quantity, and sometimes absent altogether—also hydrocyanic acid, formic acid, and ammonia, but no sulphuretted hydrogen. In fact, the hydrosulphocyanic acid separated by the hydrochloric acid is resolved into hydropersulphocyanic and hydrocyanic acids; and the latter is partially decomposed by the excess of hydrochloric acid into formic acid and ammonia. The carbonic acid and the sulphide of carbon proceed from another decomposition of part of the hydrosulphocyanic acid, in which also ammonia is produced (Völckel):

$$C^2NHS^2 + 2HO = 2CO^2 + 2HS + NH^3.$$

But sulphocyanide of potassium boiled with a very large excess of hydrochloric acid yields CO^2, HS, and NH^3 (Völckel):

$$C^2NHS^2 + 4HO = 2CO^2 + 2HS + NH^3.$$

For the action of the stronger acids in a state of dilution, *vid. Preparation of aqueous hydrosulphocyanic acid* (p. 73).

6. Sulphocyanide of potassium heated with *terchloride of antimony*, gives off bisulphide of carbon, and yields mellonide of potassium together wi tetrasulphide of antimony. (Liebig, *Handworterbuch*, 1, 123):

$$4C^2NKS^2 + SbCl^3 = 2CS^2 + SbS^4 + 3KCl + C^6N^4K.$$

7. Sulphocyanide of potassium heated with excess of *carbonate of potash* fuses into a thin liquid, which first gives off bubbles, then attains a state of tranquil fusion, and solidifies very slowly on cooling, forming a brownish yellow mass. This mass, boiled with alcohol, yields a yellow filtrate, which smells of ammonia and xanthic acid, and on cooling, deposits a large quantity of crystals of hyposulphite of potash, together with a

few needles of sulphur; but it likewise contains undecomposed sulphocyanide of potassium. (Gm.)—At a red heat, sulphocyanide of potassium gives up its sulphur to *silver* and other *metals*. (Grotthuss.)

Sulphocyanide of potassium deliquesces in the air, and dissolves abundantly in water, producing a considerable degree of cold. It likewise dissolves in alcohol, especially when hot.

Sulphocyanide of Sodium. C^2NNa,S^2.—Aqueous hydrosulphocyanic acid neutralized with carbonate of soda, and evaporated, first over the water-bath and then over oil of vitriol under a bell-jar, slowly yields rhombic tables; the salt crystallizes better from an alcoholic solution. (Meitzendorff.) Deliquescent rhombohedrons. (Porrett.) The salt, when strongly heated in the air, sometimes exhibits incandescence. Heated with moderately concentrated sulphuric acid, it first deposits yellow flakes, and gives off hydrocyanic and hydrosulphocyanic acid, then sulphurous acid, then cyanogen and sulphide of carbon, and leaves sulphate of soda.—It is very deliquescent, and dissolves very readily in water and alcohol. (Meitzendorff, *Pogg.* 56, 63.)

	Crystallized.			Meitzendorff.
2 C	12·0	....	14·78	
N	14·0	....	17·24	
Na	23·2	....	28·57	..... 27·81
2 S	32·0	....	39·41	
C^2NNaS^2	81·2	....	100·00	

The quantity of sodium obtained was somewhat too small, in consequence of moisture adhering to the crystals. (Meitzendorff.)

Sulphocyanide of Barium. C^2NBa,S^2. — 1. Formed by igniting ferrocyanide of barium with sulphur. (Berzelius, *Lehrb.*) — 2. By neutralizing hydrosulphocyanic acid with carbonate of baryta, and evaporating the filtrate, first over the water-bath, then over oil of vitriol. (Meitzendorff.)

Long shining needles. (Porrett, Berzelius, Meitzendorff.) The needles effloresce when left for some time over oil of vitriol, and between 160° and 170°, give off 12 per cent. of water. The residue, more strongly heated out of contact of air, turns brown and fuses, but crystallizes on cooling; nevertheless, small quantities of nitrogen gas and sulphur are evolved, and charcoal separated, probably by the action of water, which is still present. The salt, when heated with access of air, after dehydration, gives off sulphurous acid, nitrogen, cyanogen, and sulphide of carbon (which produces a flame of sulphur), exhibits combustion at a red heat, and leaves a mixture of sulphide of barium, sulphate of baryta, and carbonate of baryta.—The salt is deliquescent, and dissolves readily in water and in alcohol.

	Anhydrous.				*Crystallized.*				Meitz.
2 C	12·0	....	9·48		2 C	12·0	....	8·30	
N	14·0	....	11·06		N	14·0	....	9·68	
Ba	68·6	....	54·18		Ba	68·6	....	47·44	..... 47·25
2 S	32·0	....	25·28		2 S	32·0	....	22·13	
					2 Aq	18·0	....	12·45	..... 12·00
C^2NBaS^2	126·6	....	100·00		+2Aq	144·6	....	100·00	

Sulphocyanide of Strontium. C^2NSr,S^2.—Prepared like the barium-salt (2). Crystallizes, according to Porrett, in deliquescent needles; according to Meitzendorff, only in nodules, which effloresce over oil of vitriol, and slowly give up their 3 At. water when heated, leaving a residue which begins to decompose between 160° and 170°, and yields the

same products as the barium-salt,—products which are deliquescent, and dissolve readily in water and alcohol.

	Crystallized.			Meitzendorff.
Sr	44	....	34·11	..... 34·36
C^2NS^2	58	....	44·96	
3 Aq	27	....	20·93	
$C^2NSrS^2 + 3Aq$	129	....	100·00	

Sulphocyanide of Calcium. C^2NCa,S^2.—Prepared in a similar manner. Crystallizes in needles from the alcoholic solution. (Porrett.) When the aqueous solution is evaporated over oil of vitriol, indistinct crystals are obtained, which effloresce when left for some time over oil of vitriol, give off their water, but not completely, between 160° and 170°—at which temperature, in fact, decomposition begins—and behave like the barium-salt at higher temperatures. (Meitzendorff.) Deliquescent; very soluble in water and alcohol. (Porrett, Meitzendorff.)

	Crystallized.			Meitzendorff.
Ca	20	....	19·05	..... 18·29
C^2NS^2	58	....	55·24	
3 Aq	27	....	25·71	
$C^2NCa,S^2 + 3Aq$	105	....	100·00	

Sulphocyanide of Magnesium. C^2NMg,S^2. — The same mode of preparation. The dried salt has a micaceous aspect and is deliquescent. (Porrett.) The aqueous solution evaporated over oil of vitriol yields indistinct crystals, which cannot be deprived of all their water without decomposition. When dried as completely as possible, and afterwards more strongly heated in a close vessel, the salt fuses, swelling up and turning brown, gives off nitrogen and sulphuretted hydrogen, and leaves a solid pulverulent residue, from which water dissolves out sulphide of magnesium, leaving a residue of carbonate of magnesia.—The undecomposed salt dissolves readily in water and in alcohol. (Meitzendorff.)

	Crystallized.			Meitzendorff.
Mg	12	....	11·32	..... 11·85
C^2NS^2	58	....	54·72	
4 Aq	36	....	33·96	
C^2NMg,S^2	106	....	100·00	

Sulphocyanide of Yttrium.—The solution of carbonate of yttria in hydrosulphocyanic acid leaves, by spontaneous evaporation, a colourless, very deliquescent mass. (Berlin.)

Sulphocyanide of Aluminum. — Hydrate of alumina dissolves very slowly in warm hydrosulphocyanic acid. The filtrate evaporated over oil of vitriol, leaves a gummy residue, probably consisting of the neutral salt; but on evaporating the filtrate over the water-bath, hydrosulphocyanic acid goes off, and yellow flakes separate, probably consisting of a basic salt; these flakes, when left over oil of vitriol, dry up to a hard mass, sparingly soluble in acids, but soluble in boiling potash. (Meitzendorff.) Porrett obtained octohedrons permanent in the air [alum ?].

Sulphocyanide of Molybdenum.—Very soluble. (Porrett.)

Sulphocyanide of Chromium.—Very soluble. (Porrett.)

Uranous Sulphocyanide. — The light green solution of hydrated protoxide of uranium in hydrosulphocyanic acid, evaporated over oil of vitriol, leaves a dark green, crystalline mass, which, however, contains a

certain quantity of uranic sulphocyanide and likewise of uranoso-uranic oxide, which remains behind when the salt is dissolved in water. (Rammelsberg, *Pogg.* 59, 12.)

Uranic Sulphocyanide.—Easily soluble in water (Porrett); insoluble in alcohol. (Brandes.)

Sulphocyanide of Manganese.—The solution of carbonate of manganese in hydrosulphocyanic acid evaporated over oil of vitriol yields indistinct crystals, which, according to Porrett, are colourless. Between 160° and 170° they give off their water of crystallization, and then, if more strongly heated out of contact of air, fuse, turn brown, give off nitrogen, cyanogen, and a large quantity of sulphide of carbon, and after ignition, leave a blackish powder, consisting for the most part of sulphide of manganese, which dissolves in hydrochloric acid, with evolution of sulphuretted hydrogen, leaving a black powder, chiefly consisting of charcoal. (Meitzendorff.) The salt dissolves readily in water and hydrated alcohol (Meitzendorff), but is nearly insoluble in absolute alcohol. (Grotthuss.)

Sulphocyanide of Bismuth.—Hydrated oxide of bismuth (obtained by precipitating nitrate of bismuth with ammonia) dissolves in aqueous hydrosulphocyanic acid (the following compound being at the same time precipitated), and forms a yellowish red liquid, which, when evaporated over the water-bath, leaves the salt in the form of a dark yellowish red powder. (Meitzendorff.)

	At 100°.		Meitzendorff.
Bi	213	55·04	55·18
$3\ C^2NS^2$	174	44·96	45·18
$C^6N^3BiS^6$	387	100·00	100·36

Oxysulphocyanide of Bismuth.—The yellow powder precipitated on dissolving hydrated oxide of bismuth in hydrosulphocyanic acid (*Vid. sup.*) Leaves sulphide of bismuth when ignited in a close vessel, but oxide of bismuth when ignited in contact with the air. By continuous boiling with water, especially if it has not been previously dried, it is resolved into oxide of bismuth and a solution of hydrosulphocyanic acid. (Meitzendorff.)

	At 100°.		Meitzendorff.
$Bi,3CyS^2$	387	28·23	27·96
$4\ BiO^3$	948	69·14	68·49
4 Aq	36	2·63	3·55
$C^6N^3BiS^6,4BiO^3+4Aq$	1371	100·00	100·00

Sulphocyanide of Zinc.—Hydrosulphocyanic acid acts but slightly on ignited oxide of zinc, but may be neutralized by the recently precipitated carbonate. From the alcoholic solution the salt is obtained in anhydrous crystals. When fused in close vessels, it melts and turns brown, gives off nitrogen, cyanogen, sulphide of carbon, and sulphur, with violent effervescence, and leaves a dingy white porous residue, which dissolves in hydrochloric acid with evolution of sulphuretted hydrogen, leaving, however, a yellow powder.—The salt is not very soluble either in water or in alcohol. (Meitzendorff.)

	Crystallized.		Meitzendorff.
Zn	32	35·56	36·56
C^2NS^2	58	64·44	
C^2NZnS^2	90	100·00	

Ammonio-sulphocyanide of Zinc.—Sulphocyanide of zinc dissolves readily in ammonia; the solution, if evaporated with frequent addition of ammonia, yields crystals on cooling; and the mother-liquor if evaporated with fresh addition of ammonia, yields a further crop.—Rhombic prisms, with the two obtuse lateral edges making angles of 112° 45′, and the two acute lateral edges truncated; acuminated with 4 faces, derived from a rhombic octohedron, but with unequal development of the fore and hind pair, an indication that they belong to the oblique prismatic system.—Water decomposes these crystals, with separation of oxide of zinc. (Meitzendorff.)

	Crystallized.		Meitzendorff.
NH^3	17	15·89	15·68
Zn	32	29·91	30·22
C^2NS^2	58	54·20	
NH^3,C^2NZnS^2	107	100·00	

Sulphocyanide of Cadmium.—When hydrosulphocyanic acid is saturated with carbonate of cadmium, and the solution but slightly concentrated over the water-bath, this salt is deposited in the form of anhydrous, colourless, shining crystals, which are very sparingly soluble in water. (Meitzendorff.)

Ammonio-sulphocyanide of Cadmium.—Obtained like the corresponding zinc-compound.—White, shining crystals, which are decomposed by water, with separation of oxide of cadmium. (Meitzendorff.)

	Crystallized.		Meitzendorff.
NH^3	17	12·98	12·48
Cd	56	42·75	42·39
C^2NS^2	58	44·27	
NH^3,C^2NCdS^2	131	100·00	

Stannous Sulphocyanide.—Easily soluble in water. (Porrett.)

Sulphocyanide of Lead.—An aqueous mixture of acetate of lead and sulphocyanide of potassium deposits gradually at first, but more quickly when strongly agitated, shining yellow crystals of sulphocyanide of lead, which continually increase in size. The salt, heated out of contact with the air, gives off, with strong intumescence, sulphide of carbon and sulphur, leaving porous sulphide of lead which exhibits a metallic lustre. (Liebig, *Pogg.* 25, 546.) The residue of the dry distillation amounts to 88·33 per cent., in which the sulphide of lead cannot amount to more than 74 per cent. The remaining 14 per cent. consists of mellon mixed with charcoal. (Rammelsberg, *Pogg.* 56, 94.)—Sulphocyanide of lead decomposed by dry chlorine gas, yields chloride of sulphur and solid chloride of cyanogen. When gently heated with nitric acid, it is suddenly decomposed with great violence, with separation of crystalline sulphate of lead, but not of sulphur.—Sulphocyanide of lead suspended in water is but very slightly decomposed by sulphuretted hydrogen; moreover, sulphocyanide of lead introduced into the filtered liquid remains perfectly white, even if more sulphuretted hydrogen be passed through it. If the liquid be then diluted with water, the sulphocyanide of lead remains still white; but if more sulphuretted hydrogen be then passed through it, decomposition again takes place to a certain extent, till in fact the water which has been added is sufficiently saturated with hydrosulphocyanic acid to stop the action. (Völckel, *Pogg.* 58. 135.)—Jamieson (*Ann. Pharm.* 58, 264), after saturating the water with sulphuretted hydrogen

and leaving it to stand over night in a closed vessel, generally obtained complete conversion of the sulphocyanide of lead into sulphide; always indeed if the water were several times changed. [These experiments do not contradict each other; all depends on the proportion of the water to the sulphocyanide of lead. The greater this proportion, the more readily is an aqueous solution of hydrosulphocyanic acid produced of sufficient strength to prevent the further action of the sulphuretted hydrogen.]

The salt is insoluble in cold water; boiling water resolves it into a liquid which reddens litmus, and a yellow insoluble powder. (Liebig.)—According to Porrett, the salt crystallizes in rhombohedrons. (*Comp.* also Brandes, *Taschenb.* 1849, 192.) — ¶. According to Schabus (*Wien. Akad. Ber.* 1850, Januar, 108; *Jahresber.* 1850, 362), it forms crystals belonging to the oblique prismatic system. Sp. gr. 3·82. ¶

	Crystallized.		Liebig.
Pb	104	64·20	63·81
C^2NS^2	58	35·80	
C^2NPbS^2	162	100·00	

Oxysulphocyanide of Lead. — Formed by mixing an aqueous solution of sulphocyanide of potassium with subacetate of lead, or first with the neutral acetate, and then with ammonia. The abundant white, curdy precipitate becomes yellowish and pulverulent when dry. When ignited in a glass tube, it gives off a gaseous mixture containing carbonic acid; but does not yield a sublimate of sulphur. Hot nitric acid decomposes it as violently as the sulphocyanide, nearly all the lead being converted into 109·76 p. c. of sulphate, while very little dissolves in the acid liquid. With chlorine this compound behaves like the sulphocyanide. It is perfectly insoluble in water. (Liebig, *Pogg.* 15, 546.)

			Liebig.	Parnell. (*Phil. Mag. J.* 17, 250).
2 Pb	208	73·50	74·96	73·78
2 C	12	4·24		4·20
NS^2	46	16·26		
2 O	16	5·65		
H	1	0·35		0·39
C^2NPbS^2,PbO,HO	283	100·00		

Ferrous Sulphocyanide. — By dissolving iron inaqueous hydrosulphocyanic acid [whereupon a small quantity of sulphuretted hydrogen is evolved, and consequently decomposition takes place], a pale bluish green liquid is obtained, which has a sweetish, harsh taste, reddens litmus, and is itself reddened by the air, with precipitation of iron-ochre; also by chlorine, nitrous acid, &c. (Berzelius, *Lehrb.*) A similar liquid is produced by mixing the aqueous solutions of sulphocyanide of potassium and green vitriol. (Meitzendorff.)

Ferric Sulphocyanide.—The blood-red solution of recently precipitated hydrated ferric oxide in the acid crystallizes with difficulty when evaporated in the air over oil of vitriol (Porrett); according to Grotthuss, however, it does not crystallize. The mass which remains after evaporation appears black by reflected light, and is deliquescent. (Grotthuss.)—The solution is partially decomposed by evaporation over the water-bath, so that, on redissolving it in water, hydrated ferric oxide,

free from sulphocyanogen, remains undissolved; the evaporated residue, heated in a retort, gives off nitrogen, cyanogen, and sulphide of carbon, and leaves black pulverulent sulphide of iron containing carbon. By repeatedly evaporating to dryness and redissolving, a colourless liquid is formed, containing ferrous sulphocyanide and sulphuric acid. The dilute solution when boiled is more or less decolorized, with formation of sulphuric acid, and on subsequently adding an alkali to the liquid, a black precipitate is formed consisting of hydrated ferroso-ferric oxide. Hydrocyanic acid is probably formed at the same time. On boiling the aqueous solution with alcohol, it loses its colour; gives off hydrocyanic acid, with formation of a brown precipitate; and if subsequently supersaturated with an acid, yields prussian blue. (Meitzendorff.)

The solution of this compound in a small quantity of water has a deep blood-red colour; the dilute solution is reddish yellow. This solution is obtained in an impure state on mixing a ferric salt with hydrosulphocyanic acid or sulphocyanide of potassium. The liquid gradually loses its colour on exposure to sunshine (Grotthuss, A. Vogel), and is immediately decolorized by sulphuretted hydrogen, protochloride of tin, and other deoxidizing agents, which convert the ferric into a ferrous salt; but the red colour is instantly restored by the action of the air or of nitrous acid. (A. Vogel.) — Solution of chloride of gold decolorizes the liquid, and forms a yellow precipitate [of sulphocyanide of gold?] (A. Vogel.) Alkalis decolorize it by precipitating the ferric oxide. Many acids, as phosphoric, arsenic, iodic, and oxalic acid, even in small quantities, decolorize the liquid, in which case the addition of a ferric salt restores the colour. (Pelouze, *Ann. Chim. Phys.* 44, 216.) But hydrochloric acid does not destroy the colour; even in strong hydrochloric acid, a trace of sesquichloride of iron is detected by the reddening which a small quantity of sulphocyanide of potassium produces in it. Nitric acid decolorizes the liquid by destroying the sulphocyanogen; consequently the addition of a ferric salt will not restore it. (Pelouze.)—The salt is likewise soluble in absolute alcohol. (Grotthuss.)

Sulphocyanide of Cobalt.—The beautiful red solution of recently precipitated hydrated protoxide of cobalt in hydrosulphocyanic acid, becomes blue when considerably concentrated by evaporation over the water-bath, but does not yield any distinct crystals; over oil of vitriol it dries up to a yellowish brown crystalline mass, which contains 31·9 per cent. of cobalt, and probably therefore consists of $2C^2NCoS^2,Aq$. It is decomposed by heat, and dissolves readily in water and alcohol. (Meitzendorff.)—When a concentrated aqueous solution of sulphate of cobalt is precipitated by alcoholic sulphocyanide of potassium, the blue liquid filtered from the sulphate of potash leaves, on evaporation, blue prisms, which deliquesce on exposure to the air, forming first a violet, then a rose-coloured liquid, which becomes nearly colourless on the addition of a larger quantity of water, but assumes a bright blue colour on the addition of alcohol. (Grotthuss, *Gilb.* 61, 70.)

Ammonio-sulphocyanide of Cobalt.—The brown-red solution of sulphocyanide of cobalt in ammonia, if evaporated with continual addition of ammonia, and then left over oil of vitriol, dries up to a red-brown powder mixed with small crystals. The crystals, which are deliquescent, may be dissolved out by alcohol, and separate out again when the solution is left to evaporate over oil of vitriol; the brown-red powder dissolves in

water, forming a solution of a fine red colour. Both the crystals and the powder contain ammonia and sulphocyanide of cobalt. (Meitzendorff.)

Sulphocyanide of Nickel.—The green solution of recently precipitated carbonate of nickel in hydrosulphocyanic acid becomes syrupy when left to evaporate spontaneously, but does not crystallize. Over oil of vitriol it dries up to a yellowish crystalline powder containing 31·82 p. c. water, probably therefore $=2C^2NNiS^2,Aq$. This powder gives off its water at 150°, and if more strongly heated in a close vessel, evolves nitrogen, cyanogen, sulphide of carbon, and sulphur, leaving a brown powder; this residue dissolves partially in hydrochloric acid, with evolution of sulphuretted hydrogen, and there is left a black residue, which when heated in a spoon, burns away with a glimmering light and leaves oxide of nickel. (Meitzendorff.)

Ammonio-sulphocyanide of Nickel. — The blue solution of the preceding salt in ammonia, if evaporated over the water-bath, yields on cooling, blue crystals, which effloresce slowly, and are decomposed by water, with separation of oxide of nickel and evolution of ammonia. (Meitzendorff.)

			Meitzendorff.
$2\ NH^3$	34·0	27·99	27·15
Ni	29·5	24·28	24·80
C^4NS^2	58·0	47·73	
NH^3,C^2NNiS^2	121·5	100·00	

Cuprous Sulphocyanide. C^2NCu^2,S^2. — Produced by digesting hydrated cuprous oxide with hydrosulphocyanic acid, or with a mixture of aqueous sulphocyanide of potassium and hydrochloric acid not in excess (Berzelius);—by precipitating a cuprous salt with sulphocyanide of potassium;—by precipitating a dilute solution of blue vitriol—mixed with green vitriol (2 pts. blue to 3 pts. green vitriol) (Porrett), or with sulphurous acid—with sulphocyanide of potassium. With green vitriol:

$$KCyS^2 + 2(CuO,SO^3) + 2(FeO,SO^3) = Cu^2CyS^2 + KO,SO^3 + Fe^2O^3,3SO^3.$$

With sulphurous acid:

$$KCyS^2 + 2(CuO,SO^3) + SO^2 = Cu^2CyS^2 + KO,3SO^3.$$

But even without the addition of a deoxidizing agent, hydrated cupric oxide or cupric carbonate treated with hydrosulphocyanic acid sufficiently diluted, or a dissolved cupric salt treated with sufficiently dilute sulphocyanide of potassium, yields, after a while, cuprous sulphocyanide (Claus, *J. pr. Chem.* 15, 401; Meitzendorff); according to the latter, also, the product in this case is not white but yellowish (*comp.* Cupric Sulphocyanide; decomposition by water).—To purify the precipitate obtained with green vitriol, from ferric oxide, and render it perfectly white, it must be washed first with dilute sulphuric acid, and then with water. (Liebig.)

			Claus (at 115°).	Meitzendorff (at 115°).	Porrett.
2 Cu	64	52·46	50·3	51·21	56·13
C^2NS^2	58	47·54	46·7	47·25	
HO			3·0	1·54	
$C^2NCu^2S^2$	122	100·00	100·0	100·00	

The salt therefore still retains water at 115°, but much less than 1 At. — It may be completely dehydrated by heating it in an open dish till it begins to turn brown. (Liebig.)

Cuprous sulphocyanide, when subjected to dry distillation, is resolved into sulphide of carbon, and a residue consisting of mellon and disulphide of copper; at a stronger heat, sulphur is driven off, and there remains mellonide of copper, which requires a still higher temperature to decompose it (Liebig, *Ann. Pharm.* 50, 347):

$$4C^2NCu^2S^2 = 2CS^2 + 4Cu^2S + C^6N^4;$$

then probably:

$$4Cu^2S + C^6N^4 = Cu^2C^6N^4 + 3Cu^2S + S.$$

When the salt, after being dried at 130°, is more strongly heated in a retort, it turns brown; gives off, first small quantities of gas and free sulphur, then a large quantity of sulphide of carbon, together with nitrogen and cyanogen gas, and leaves a black powder mixed with crystalline spangles. Of this residue hydrochloric acid dissolves a small quantity, with evolution of sulphuretted hydrogen; nitric acid a larger quantity, with formation of sulphuric acid; and aqua-regia still more, leaving a residue of mellon. Hence the ignited residue appears to be a mixture of mellon and sulphide of copper. (Meitzendorff.) At 200°, the salt gives off but a small quantity of water without further decomposition; at a stronger heat, it blackens, gives off hydrosulphocyanic acid, cyanogen, sulphide of carbon, free sulphur, and carbonate of ammonia, and leaves a black mass, which, when treated with nitric acid, yields a copper solution, containing sulphuric acid, together with a yellow residue consisting of copper and sulphur [and mellon ?]. (Claus.) The dried salt, when subjected to dry distillation, gives off 6·67 p. c. water (12·5 p. c. according to Grotthuss), then sulphur, sulphide of carbon, cyanogen, and nitrogen; and sometimes also a small quantity of hydrosulphocyanic acid. If mixed, before heating, with half its weight of copper filings, it gives off a large additional quantity of gas, which behaves like cyanogen. (Porrett.) — Cuprous sulphocyanide burns with a blue flame when heated in the air. — Mixed with 5 pts. of chlorate of potash, it detonates violently by percussion, heat, or electricity, or when touched with oil of vitriol. (Porrett.) It is decomposed by digestion with chlorate of potash and hydrochloric acid. (Grotthuss.) — Strong nitric acid blackens the salt with effervescence, converting it into cupric sulphocyanide, then dissolves this new compound, with increasing effervescence, and forms a green liquid, containing the sulphur in the form of sulphuric acid. (Claus, Meitzendorff.)—Hot oil of vitriol forms cupric sulphate, with evolution of sulphurous acid; if the quantity of oil of vitriol added be very small, a black substance separates out, partly consisting of sulphide of copper. (Meitzendorff.)—Cold strong hydrochloric acid exerts but a slight action on this compound; but the same acid when hot, dissolves it, separating dichloride of copper, if the quantity of acid added is but small. (Meitzendorff.) According to Grotthuss, hydrochloric acid [probably dilute ?] exerts no action, even at a boiling heat. — Sulphuretted hydrogen decomposes cuprous sulphocyanide, forming sulphide of copper, but only when water is present. (Porrett.) Cuprous sulphocyanide suspended in water behaves with sulphuretted hydrogen in the same manner as sulphocyanide of lead (p. 87), excepting that the decomposition is still more partial, so that the salt merely assumes a brownish tint; the decomposition ceases as soon as the water has become charged with a certain small quantity of hydrosulphocyanic acid. (Völckel.) On the other hand, Jamieson found with this subtance the same relations as with

sulphocyanide of lead (p. 87).—Aqueous fixed alkalis decompose cuprous sulphocyanide, separating hydrated cuprous oxide, and forming a sulphocyanide of the alkali-metal. (Porrett, Claus.) Cuprous sulphocyanide does not dissolve in water, or in those acids which do not decompose it. (Porrett.) When recently precipitated, it dissolves completely in aqueous ammonia, but when dry, it leaves a yellow basic salt; the solution is colourless, but turns blue on exposure to the air. (Claus.)

¶ *Cuproso-cupric Sulphocyanide.* $C^4N^2Cu^3S^4 = C^2NCu^2S^2, C^2NCuS^2$, *Kupferrhodanür-rhodanid.* — When black cupric sulphocyanide is dissolved in a warm alcoholic solution of sulphocyanide of potassium, and the liquid evaporated at a gentle heat, this compound separates in the form of an orpiment-coloured precipitate. The liquid is then to be filtered, and the precipitate washed, first with alcohol and then with water, to remove the sulphate of potash which has been formed. It forms an orpiment-coloured, amorphous powder, which is not acted upon by water, is insoluble in sulphocyanide of potassium, and is decomposed by potash-ley, with formation of sulphocyanide of potassium. Hydrochloric acid exerts no action upon it, not even on the addition of chlorate of potash. Strong nitric acid, on the contrary, acts violently upon it, producing cupric sulphocyanide. (Hull, *Ann. Pharm.* 76, 93.)

			Hull.
3 Cu	96·0	44·95	45·28
2 C^2NS^2	116·0	55·05	53·62
$C^2NCu^2S^2, C^2NCuS^2$	212·0	100·00	100·00

The same compound appears to be formed when dry cupric sulphocyanide is gently heated on platinum foil over a spirit-lamp; sulphide of carbon, cyanogen, and other volatile products are then given off, and the mass rapidly assumes a brownish yellow colour. (Hull.) ¶

Cupric Sulphocyanide.—1. Obtained by immersing hydrated cupric oxide or cupric carbonate in excess of concentrated hydrosulphocyanic acid. (Claus, Meitzendorff.) — 2. By adding sulphocyanide of potassium, not in excess, to a concentrated aqueous solution of a cupric salt. (Claus, Meitzendorff.) If the sulphocyanide of potassium be in excess, a grey precipitate is formed. (Claus.) When less concentrated solutions are used, the precipitate turns grey, being contaminated with cuprous sulphocyanide; the supernatant liquid exhibits a brownish colour, due to the presence of a small quantity of cupric sulphocyanide remaining in solution. (Meitzendorff.) Washing with water would decompose the precipitate (Claus,); it must, therefore, be pressed between paper and dried over oil of vitriol. (Meitzendorff.) When dilute solutions are used, no precipitate is obtained, but a yellowish green mixture is formed, from which sulphurous acid, sulphite of potash, protochloride of tin, green vitriol, and dichloride of copper dissolved in hydrochloric acid, throw down white cuprous sulphocyanide. (Porrett.) — ¶ 3. According to Hull (*Ann. Pharm.* 76, 94), the best mode of preparing this compound is to add a slight excess of sulphuric acid to a moderately concentrated solution of sulphocyanide of potassium previously freed from air by boiling and left to cool, and then to add a saturated solution of cupric sulphate also freed from air. The compound then separates in the form of a black crystalline precipitate, which may easily be washed with water freed from air and cooled. ¶

Velvet-black powder, inodorous when dry. (Claus, Meitzendorff.)

			Meitzendorff.	Claus.
Cu	32	35·56	35·56	35·9
C^2NS^2	58	64·44	64·21	59·7
C^2NCuS^2	90	100·00	99·77	95·6

The salt analyzed by Meitzendorff had been dried at 100° over oil of vitriol. Both Meitzendorff and Claus determined the amount of sulphocyanogen from that of the sulphate of baryta obtained from it.

The salt decomposes at a temperature a little above 100°; when subjected to dry distillation, it gives off a small quantity of hydrosulphocyanic acid, then sulphide of carbon, then a tolerably large quantity of free sulphur, and leaves a brownish residue, which, when treated with aqua-regia, leaves a yellow body resembling mellon. (Claus.) Accordingly, this decomposition yields but little cyanogen, but large quantities of nitrogen and sulphide of carbon, the residue being a black-brown powder, mixed with crystalline spangles, and consisting of sulphide of copper and a body resembling mellon. The salt, when immersed in nitric acid, first turns white and then dissolves with formation of sulphuric acid. It dissolves in warm oil of vitriol, first, however, turning white; in a smaller quantity of oil of vitriol it dissolves with separation of a black substance containing sulphide of copper. It does not dissolve in cold hydrochloric acid; but that acid, when hot, dissolves it, first turning it white. (Meitzendorff.) — When treated with a small quantity of water, it is converted into a grey mixture of cuprous and cupric sulphocyanide; a larger quantity of water converts it completely into white cuprous sulphocyanide. The green aqueous solution thereby formed contains hydrosulphocyanic acid. Hence the compound, when exposed to moist air, takes up water with avidity, and exhales the odour of hydrosulphocyanic acid. (Claus.) The dried salt is less quickly decomposed by water; the decomposition is, however, accelerated by heat. The water takes up hydrocyanic and sulphuric acids as well as hydrosulphocyanic acid, the relative quantities of the several products of the decomposition being represented with sufficient accuracy by the following equation (Meitzendorff):

$$12C^2NCuS^2 + 6HO = 2SO^3 + C^2NH + 5C^2NHS^2 + 6C^2NCu^2S^2.$$

Alcohol produces the same decomposition as water, but less quickly; at a boiling heat, however, it acts more readily than when cold. (Claus.) A highly concentrated solution of sulphocyanide of potassium dissolves the salt with effervescence and evolution of hydrosulphocyanic acid, forming a brown liquid from which water throws down cuprous sulphocyanide. Aqueous solution of potash separates from the salt a yellow-green mixture of hydrated cuprous and cupric oxides. Ammonia dissolves the salt, forming a deep blue solution, and leaving the same basic salt as in the case of cuprous sulphocyanide. (Claus, *J. pr. Chem.* 15, 401.)

Cuprous Sulphocyanide with Ammonia.—The solution of cuprous sulphocyanide in warm ammonia deposits thin grey, crystalline laminæ, as it cools. If the bluing of the liquid be not prevented by keeping it from the air, the laminæ exhibit a steel-blue colour when viewed through it. (Meitzendorff.)

Cupric Sulphocyanide with Ammonia. — Obtained by dissolving cupric sulphocyanide in ammonia, or by digesting the cuprous sulphocyanide

with ammonia in contact with the air; evaporating the solution with frequent addition of ammonia; and finally, either leaving it to evaporate over oil of vitriol or mixing it with absolute alcohol. In both cases, small blue needles are produced, which, when moderately heated in a retort, fuse with copious formation of bubbles, and yield, first a crystalline sublimate of sulphocyanide of ammonium, then nitrogen gas, cyanogen, and free sulphur, and leave sulphide of copper, together with a substance resembling mellon. (Meitzendorff.)

			Meitzendorff.
NH^3	17	15·89	16·01
Cu	32	29·91	30·54
C^2NS^2	58	54·20	
NH^3,C^2NCuS^2	107	100·00	

Mercurous Sulphocyanide. — Formed by precipitating mercurous nitrate with sulphocyanide of potassium. (Wöhler, *Gilb.* 69, 272.) The solutions must be very dilute. (Claus, *J. pr. Chem.* 15, 406.) The white precipitate, if heated after drying, to a temperature short of redness, swells up suddenly, giving off nitrogen gas, vapour of sulphide of carbon, and vapour of mercury; and forms a very bulky, frothy mass, consisting of graphite-like lamina, and containing carbon and nitrogen [a mixture of mellon and sulphide of mercury]. This mass, when more strongly heated, yields cinnabar; it is not attacked by carbonate of potash, or by most acids, even in a high state of concentration; but aqua-regia first colours it yellowish white, and then dissolves it, with evolution of nitric oxide. (Wöhler.) Claus, on heating this substance, obtained sulphide of carbon, cyanogen, sulphide of mercury, and a residue of mellon. [Free mercury must, however, likewise distil over; for the quantity of sulphur is not sufficient to form both sulphide of carbon and sulphide of mercury].

Mercurous sulphocyanide is very little attacked by nitric acid, but very readily by aqua-regia, even without the aid of heat. (Claus.) Hydrochloric or hydrosulphuric acid transforms it into chloride or sulphide of mercury and hydrosulphocyanic acid. (Wöhler.)

			Claus.
2 Hg	200	77·52	77·19
C^2NS^2	58	22·48	22·73
$C^2NHg^2S^2$	258	100·00	99·92

Mercuric Sulphocyanide. — An aqueous solution of hydrosulphocyanic acid, saturated with mercuric oxide, yields, by spontaneous evaporation, colourless needles, united in radiated masses, and having a sharp metallic taste. These crystals contain water, and when heated, give off with great violence, nitrogen gas, sulphide of carbon, a gas having a peculiar odour; and, likewise (according to *Berzelius' Lehrbuch*) carbonate of ammonia; afterwards they yield a sublimate of cinnabar, and a yellowish or brownish residue [probably containing mellon]. (Berzelius, *Schw.* 31, 56.)

Mercuric Oxysulphocyanide.—Ammonia, added to the aqueous solution of the compound of mercuric sulphocyanide with sulphocyanide of potassium, throws down a lemon-yellow powder. This powder, when heated to 180°, decomposes suddenly with a slight explosion, whereby it is partly projected from the vessel, with production of a grey smoke and blue flame, and emission of sulphurous acid, after which it gives off mercury and

sulphide of mercury, and ultimately leaves a residue of mellon. When mixed with burnt lime, it may be heated without explosion or evolution of ammonia; but with hydrate of lime, it yields carbonate of ammonia, like other sulphocyanides. Aqueous acids and alkalis act but slightly upon it; nevertheless, alkalis abstract a small quantity of the sulphocyanogen, and boiling potash changes the colour of the powder, though it does not eliminate ammonia. (Claus.)

			Claus.
3 Hg	300	80·21	79·8
C^2NS^2	58	15·51	15·6
2 O	16	4·28	
$C^2NHgS^2,2HgO$	374	100·00	

Of the same nature is doubtless also the lemon-yellow amorphous body which Berzelius (*Schw.* 31, 57) obtained by continuous digestion of aqueous hydrosulphocyanic acid with excess of mercuric oxide, and which he regarded as mercurous sulphocyanide. This substance dissolves in hydrochloric acid, and is precipitated unchanged from the solution by water. It is not decomposed by potash-ley or by digestion with the greater number of acids; but when treated for some time with strong aqua-regia, it undergoes decomposition.

Sulphocyanide of Mercury and Potassium. — Formed in the decomposition of mercurous nitrate or calomel by concentrated sulphocyanide of potassium, half of the mercury being separated in the free state:

$$2Hg^2Cl + 3KCyS^2 = 2KCl + 2Hg + KCyS^2,2HgCyS^2.$$

To prepare the compound, therefore, calomel and sulphocyanide of potassium are triturated together in equal quantities, with gradual addition of water; the liquid separated by filtration from the black mixture of mercury and undecomposed calomel, and evaporated till it crystallizes; and the resulting cubes and octohedrons of chloride of potassium separated from the yellow tables of the double sulphocyanide, which latter, when purified by recrystallization from boiling alcohol, are converted into snow-white, heavy needles, having a pearly lustre and united in radiated masses. The salt, when heated to 180°, turns yellow, and afterwards black; at a higher temperature, it gives off sulphide of carbon, free sulphur, and sulphide of mercury, and finally leaves sulphocyanide of potassium, probably mixed with mellonide. Ammonia, added to the aqueous solution of this compound, throws down lemon-yellow mercuric oxysulphocyanide; potash forms an orange-yellow precipitate of mercuric oxide, to which, however, a trace of sulphocyanogen obstinately adheres. The salt dissolves with difficulty in cold, more easily in hot water; very easily in aqueous sal-ammoniac or chloride of potassium; readily in alcohol, especially at a boiling heat, and likewise in ether. (Claus, *J. pr. Chem.* 15, 407.)

			Claus.
K	39·2	9·49	9·1
2 Hg	200·0	48·40	47·1
3 C^2NS^2	174·0	42·11	41·8
Aq			1·0
$C^2NKS^2,2C^2NHgS^2$	413·2	100·00	

The crystals examined by Claus lost 1 per cent. of water when strongly heated.

Cyanide of Mercury with Sulphocyanide of Potassium. — Formed by dissolving 1 At. sulphocyanide of potassium and 2 At. cyanide of mercury in hot water, and cooling the solution. Broad laminæ and long, white, shining needles. (C. Böckmann, *Ann. Pharm.* 22, 153.) This is doubtless identical with the silvery-lustrous salt slightly soluble in cold, but very easily soluble in hot water, previously described by Porrett. (*Schw.* 17, 288.)

Crystallized.			Böckmann.
K	39·2	11·22	11·06
2 Hg	200·0	57·27	57·22
3 C^2N	78·0	22·34	
2 S	32·0	9·17	9·11
$C^2NKS^2,2C^2NHg$	349·2	100·00	

Cyanide of Mercury with Sulphocyanide of Barium. — The solution of carbonate of baryta in hydrosulphocyanic acid, mixed warm with cyanide of mercury, yields small nacreous laminæ on cooling. (Böckmann.)

Crystallized.			Böckmann.
Ba	68·6	18·12	18·00
2 Hg	200·0	52·83	51·80
3 C^2N	78·0	20·60	
2 S	32·0	8·45	8·45
$C^2NBaS^2,2C^2NHg$	378·6	100·00	

Cyanide of Mercury with Sulphocyanide of Calcium.—Obtained in a similar manner.—White shining laminæ. (Böckmann.)

Crystallized.			Böckmann.
Ca	20	6·06	5·82
2 Hg	200	60·61	59·93
3 C^2N	78	23·63	
2 S	32	9·70	9·13
$C^2NCaS^2,2C^2NHg$	330	100·00	

Cyanide of Mercury with Sulphocyanide of Magnesium.—Prepared in a similar manner. White crystalline powder. (Böckmann.)

Crystallized.			Böckmann.
Mg	12	3·73	3·96
2 Hg	200	62·11	61·67
3 C^2N	78	24·22	
2 S	32	9·94	10·10
$C^2NMgS^2,2C^2NHg$	322	100·00	

Sulphocyanide of Silver. C^2NAg,S^2. — Hydrosulphocyanic acid and sulphocyanide of potassium yield a white, curdy precipitate with nitrate of silver. (Porrett.)—Sulphocyanide of silver blackens by exposure to light more quickly than the chloride. (Grotthuss.) Also, when dried for some time at 200°, and then more strongly heated, it still gives off a small quantity of hydrosulphocyanic acid. (Völckel.) — Dry chlorine gas acts upon dry sulphocyanide of silver even at ordinary temperatures, colouring it scarlet, causing an evolution of heat, and forming chloride of sulphur, fixed chloride of cyanogen, and a sulphocyanogen-compound; if again heated in the atmosphere of chlorine, it turns yellowish red, and yields a yellowish red sublimate, small in quantity, however, because the decomposition of the sulphocyanide of silver is but imperfect.—This yellowish red sublimate, treated with potassium, yields sulphocyanide of

potassium, the action being accompanied with appearance of fire and evolution of a brown gas; it is insoluble in water, and in all acids excepting nitric acid and oil of vitriol. (Liebig, *Pogg.* 15, 546.)—If the chlorine gas has been previously freed, as completely as possible, from water and hydrochloric acid, it forms, with sulphocyanide of silver, nothing but chloride of sulphur, chloride of cyanogen, and chloride of silver. (Völckel, *Ann. Pharm.* 43, 99):

$$3C^2NAgS^2 + 12Cl = 6SCl + 3AgCl + C^6N^3Cl^3.$$

Chlorine-water decomposes sulphocyanide of silver, forming chloride of silver, sulphur, ammonia, and carbonic acid. (Grotthuss, *Schw.* 20, 240.) Sulphocyanide of silver dissolves in ammonia. It does not dissolve in nitric acid, nitrate of silver, or hydrosulphocyanate of ammonia. (Aschoff, *N. Br. Arch.* 3, 18.)

			Parnell. (*Phil. Mag. J.* 17, 250.)
2 C	12	7·23	7·20
N	14	8·43	
Ag	108	65·06	
2 S	32	19·28	
H			0·05
C^2NAg,S^2	166	100·00	

¶ *Sulphocyanide of Silver and Potassium.*—A solution of sulphocyanide of silver in sulphocyanide of potassium, saturated white hot, deposits, if left to stand over sulphuric acid, colourless, shining crystals, which, when freed from the mother-liquor, are permanent in the air. The crystals belong to the rhombic system and form modified rhombic octohedrons. Water resolves them into sulphocyanide of potassium and crystalline sulphocyanide of silver. They melt at 140°, and are decomposed at a higher temperature. (Hull, *Ann. Pharm.* 76, 96.)

			Hull.
K	39·2	14·89	15·13
Ag	108·0	41·03	39·95
2 C^2NS^2	116·0	44·08	44·01
C^2NKS^2,C^2NAgS^2	263·2	100·00	99·09

Recently precipitated cyanide of silver is dissolved in large quantity by a concentrated solution of cyanide of potassium. Water added to the solution throws down crystalline sulphocyanide of silver. No definite compound could be isolated from this solution. Recently precipitated chloride of silver also dissolves abundantly in solution of sulphocyanide of potassium. (Hull.) ¶

Sulphocyanide of Gold.—Sulphocyanide of potassium, but not free hydrosulphocyanic acid, forms, with solution of chloride of gold, a flesh-coloured precipitate easily soluble in ammonia. The precipitate, treated with hydrochloric acid, assumes a dark purple colour; with alkalis it turns yellow and gives up some of its sulphocyanogen; sulphocyanide of potassium dissolves it, forming a purple solution. (Grotthuss.)

Bisulphocyanide of Platinum.—Yellowish white, insoluble in water, but soluble in aqueous acids and aqueous metallic chlorides, from which solutions it is precipitated in yellowish white flakes by water. (Grotthuss.)

Protosulphocyanide of Palladium.—Readily soluble in water. (Porrett.)

Sulphuretted Cyanogen-compounds of doubtful constitution, perhaps to be regarded as Copulated Compounds.

To this head belong the following compounds, expressed in empirical formulæ.

Hydrothio-sulphoprussic acid $= C^2NH^2S^3$.
Hydranzothin $= C^2NH^2S^4$.
Hydropersulphocyanic acid $= C^2NHS^3$.
Pseudosulphocyanogen (composition not yet determined).
Hydrothiocyanic acid $= C^{10}N^5H^6S^{12}O^2$.
Sesquihydrosulphate of Cyanogen $= C^4N^2H^3S^3$.
Bihydrosulphate of Cyanogen $= C^2NH^2S^2$.

Hydrothio-sulphoprussic Acid.

$C^2NH^2S^3 = C^2NH,S^2HS = C^2AdS,S^2 = C^2Ad^2S^2 + 2CS^2$.

ZEISE (1824) *Schw.* 41, 100, and 170.—*Ann. Pharm.* 48, 95; also *J. pr. Chem.* 30, 292.

Formation, Preparation, and Properties.—The ammonia-salt of this acid is formed by the action of sulphide of carbon on alcohol saturated with ammoniacal gas (II. 205); also by treating hydrosulphocarbonate of ammonia with alcohol (II. 463).—The solution of this salt in 3 pts. of water is mixed with sulphuric or hydrochloric acid diluted with twice its quantity of water, then quickly diluted with a larger quantity of water, whereby the separation of the hydrothio-sulphoprussic acid is effected.—This compound is a transparent and colourless oil (if the quantity of water added be not exactly that which is required, the oil is coloured and opaque). It remains permanent for a few minutes under the acid liquid, but decomposes during the attempt to separate it from that liquid. (Zeise.)

Calculation, according to Zeise's experiments.

2 C	12	15·79
N	14	18·42
2 H	2	2·63
3 S	48	63·16
$C^2NH^2S^3$	76	100·00

According to Zeise, it is $= C^2NHS^2,HS$, *i.e.*, hydrosulphocyanic or sulphoprussic acid + Hydrosulphuric acid; according to Berzelius (*Lehrb.*), and Völckel (*Pogg.* 63, 99), also $C^2NHS^2 + HS$, the C^2NH being supposed to be, not hydrocyanic acid, but a hypothetical radical, *Urene*, so that the compound contains 1 At. hydrosulphuric acid united, not with hydrosulphocyanic acid, but with 1 At. *Sulphide of Urene;* according to Laurent (*Revue scient.* 19, 151), it is C^2AdS,S^2. The formula $C^2Ad^2,S^2 + 2CS^2$ derives a degree of probability higher than that of any of the rest, from the facility with which the compound gives off sulphide of carbon.

Decompositions. 1. When sulphuric acid, but slightly diluted, is poured upon the crystallized ammonia-salt of this acid, a white, tallowy

substance separates out, insoluble in water, but decomposing, after a while, when left in contact with that liquid. When sulphuric or hydrochloric acid, diluted with 8 times its amount of water, is mixed with the salt dissolved in 12 parts of water, the mixture, which is clear at first, exhibits, after a few minutes, a turbidity which extends from below upwards, disappears on the addition of more water, reappears after a while, disappears again on a still further addition of water, reappears after another interval, and so forth, till the dilution has been carried to a great extent; but the greater the degree of dilution attained, the longer is the interval which elapses before the turbidity appears. If the liquid be then left for 12 hours in a well stopped bottle, sulphide of carbon separates out, and the liquid then contains an ammoniacal salt, and probably also hydrocyanic acid:

$$2C^2NH^2S^3 = C^2NH + NH^3 + 2CS^2 + S^2.$$

The S^2 appear to remain in solution. (Zeise.)—Chlorine water and ferric salts added to the aqueous solution of hydrothiosulphoprussiate of ammonia, supersaturated with an acid, throw down white shining scales of hydranzothin $C^2NH^2S^4$ (Zeise). vid. *Hydranzothin.*

The compounds which hydrothio-sulphoprussic acid forms with salifiable bases—called *Sulphocyanhydrates* by Berzelius, have probably the composition $C^2NHMS^3 = C^2NHS^2,MS$, being made up, as it were, of 1 At. of a sulphide, with 1 At. hydrosulphocyanic acid. The alkaline compounds are colourless, those of the heavy metals sometimes of a light, sometimes of a dark yellow, rarely white. The alkaline salts dissolved in water are converted, at a temperature near 100°, into sulphocyanides of the alkali-metals, with separation of sulphur. The alkaline salts dissolved in alcohol and exposed to the air, are converted into sulphocyanides, with separation of sulphur-crystals, even at ordinary temperatures:

$$C^2NHKS^3 + O = C^2NKS^2 + S + HO.$$

With lead-salts and mercuric salts they form white precipitates, which spontaneously resolve themselves into sulphides and hydrosulphocyanic acid, becoming first yellow, then reddish, then black; with copper and silver salts they form yellow precipitates, which undergo the same decomposition on the application of heat:

$$C^2NHCuS^3 = CuS + C^2NHS^2.$$

These precipitates undergo a similar decomposition when treated with a solution of potash. (Zeise.)

$$C^2NHCuS^3 + KO = CuS + C^2NKS^2 + HO.$$

Hydrothio-sulphoprussiate of Ammonia, Hydrothio-cyanide of Ammonium. $NH^3,C^2NH^2S^3 = C^2NH(NH^4)S^3$?—Absolute alcohol is completely saturated at 10° or 12° with ammoniacal gas; 100 pts. of the solution mixed in a wide-mouthed glass with 16 pts. of sulphide of carbon dissolved in 40 parts of absolute alcohol; the glass immediately closed air-tight; the mixture shaken up, and left to itself for a quarter of an hour at 15°. From the liquid, which gradually turns brown, hydrosulphocarbonate of ammonia crystallizes out first,—then after half an hour, a continually increasing quantity of hydrothio-sulphoprussiate of ammonia. If the solution be too much cooled, a larger quantity of sulphocarbonate is formed. An hour and a half after mixing, the liquid is poured through a filter wetted with alcohol into another similar glass, the vessel quickly and

accurately closed, and left to stand, first at + 15°, then at temperatures between + 8° and 0°. In 24 hours, the greater part of the hydrothio-sulphoprussiate of ammonia crystallizes out; the quantity which separates afterwards is but small, and, moreover, a portion may be decomposed. Hence, after the lapse of from 30 to 48 hours, the liquid may be decanted; the salt washed several times with a very small quantity of ice-cold alcohol (then also with ether, according to Berzelius), till the liquid which runs through no longer exhibits any perceptible colour; and the crystals pressed between filtering paper. To render the salt permanent, it must be further dried in vacuo, over chloride of calcium. If it contains hydrosulphocarbonate of ammonia, it must be exposed for a few minutes to the air, whereupon the hydrosulphocarbonate will partly volatilize, partly deliquesce and sink into the paper. If the salt produces any turbidity on being dissolved in water, it contains sulphide of carbon. If it forms a red instead of a white precipitate with lead-salts, it contains hydrosulphocarbonate of ammonia; if the liquid above the lead-precipitate reddens ferric-salts immediately after its formation, it contains hydrosulphocyanate of ammonia.

Large, shining crystals, the colour of which inclines sometimes to lemon-yellow, sometimes to orange-yellow; neutral to vegetable colours; inodorous when recently formed; smells of sulphuretted hydrogen and ammonia after exposure to the air. (Zeise.)

Calculation, according to Zeise's hypothesis.

2 C	12		12·90
2 N	28		30·11
5 H	5		5·38
3 S	48		51·61
$NH^3,C^2NH^2S^3$	93		100·00

The crystals are anhydrous.

The salt, when heated, melts with intumescence, turns white, gives out at 150° a large quantity of sulphuretted hydrogen gas, probably mixed with cyanogen and nitrogen,—also sulphide of carbon, hydrosulphocarbonate of ammonia, and a white needle-shaped salt, which appears to be hydrocyanate of ammonia. At 200°, it becomes continually browner and more viscid, gives off less and less of the above-named substances, and finally solidifies, forming a brown [mellonoïdal] substance.—If kept in the undried state, it is resolved, in the course of a few weeks, into sulphuretted hydrogen and hydrosulphocyanate of ammonia, if the air be excluded, but, in the contrary case, it yields sulphur, water, and hydrosulphocyanate of ammonia. A similar decomposition takes place when an alcoholic solution of the salt is exposed to the air; such a solution, when heated, yields hydrosulphate, sulphite, and sulphate of ammonia, together with a deposit of sulphur, &c.

The salt becomes moist on exposure to the air, dissolves somewhat abundantly in water, forming a yellowish liquid, which is colourless when dilute. It dissolves very slowly in cold, more quickly in warm alcohol, still more slowly in ether, and not at all in rock-oil. (Zeise.)

Hydrothio-sulphocyanide of Potassium. C^2NHKS^3?—Formed by adding to a concentrated aqueous solution of hydrosulphoprussiate of ammonia, a quantity of potash not quite sufficient to decompose it completely, placing the slightly heated mixture in vacuo to drive off the ammonia, adding to the residue, which now no longer exhibits an alkaline reaction, a small additional quantity of potash, again leaving the ammonia to

evaporate in vacuo at a gentle heat, and repeating this process till the residue permanently reddens tumeric paper: the excess of potash is to be neutralized by the addition of a small quantity of ammoniacal salt, and evaporation in vacuo. The liquid thus obtained dries up in vacuo over chloride of calcium, to a white crystalline mass, soluble in water and alcohol. In the state of aqueous solution, the salt decomposes at a temperature below its boiling point, becoming turbid, depositing sulphur, and yielding a solution of sulphocyanide of potassium; in the alcoholic solution, the same conversion takes place in a few days, with formation of sulphur-crystals. (Zeise, *Schw.* 41, 192.)

The *Barium-salt* may be prepared in the same manner as the potassium-salt. (Zeise.)

The *Calcium-salt* is also prepared in a similar manner, using milk of lime, precipitating the excess of lime by alcohol, and leaving the filtrate to evaporate to dryness in vacuo. (Zeise.)

Hydrothio-sulphocyanide of Zinc.—The aqueous solution of the ammoniacal salt forms with sulphate of zinc, a white, very slowly increasing precipitate, in which in the course of some days, a few olive-green pyramidal crystals are formed, apparently consisting of the zinc-salt. (Zeise.)

Hydrothio-sulphocyanide of Lead.—The white flocculent precipitate which the ammoniacal salt forms with lead-salts decomposes completely in five minutes into pulverulent sulphide of lead and hydrosulphocyanic acid, assuming in the course of the decomposition, first a yellowish, then a reddish, then a greyish, and ultimately a black colour. The precipitate, while recently formed and still white, dissolves in excess of nitrate of lead, and the solution forms a yellow precipitate with copper-salts. (Zeise, *Schw.* 41, 174 and 199.)

Hydrothio-sulphocyanide of Iron?—Ferric salts form with the ammonia-salt a black precipitate, which, however, is quickly resolved into ferrous sulphocyanate which dissolves, and scales of hydranzothin. (Zeise.)

Hydrothio-sulphocyanide of Copper—The ammonia-salt forms a yellow flocculent precipitate with cupric salts. This precipitate, after being washed with water and dried, does not change by keeping; but by boiling for some time with water, it is resolved into protosulphide of copper and hydrosulphocyanic acid, and when caustic potash-ley is poured upon it, into protosulphide of copper and sulphocyanide of potassium (p. 99). (Zeise.)

Hydrothio-sulphocyanide of Mercury.—The white precipitate which the ammonia-salt forms with mercuric salts, decomposes nearly as fast as the lead-compound, becoming first yellow, then red, and then black. (Zeise).

Hydrothio-sulphocyanide of Silver.—The ammonia-salt forms a yellow precipitate with very dilute solutions of silver-salts. (Zeise.)

Hydranzothin. $C^2NH^2S^4 = C^4Ad^2S^2,S^6 = C^2Ad^2,S^4 + 2CS^2$.

ZEISE, *Schw.* 41. 185 and 195.—*Ann. Pharm.* 47, 36; 48, 95; also *J. pr. Chem.* 29, 382, and 30, 292.

Doppeltschwefelwasserstoff-Schwefelcyan (Zeise), *Dreifachschwefeluren-Schwefelwasserstoffsäure* (Völckel), *Schwefelcyanbisulfhydrat.*—Discovered and examined by Zeise in 1824.

Formation. 1. By mixing aqueous hydrothio-sulphoprussiate of ammonia with chlorine water, hydrosulphocyanate of ammonia and sal-ammoniac being formed at the same time:

$$2(NH^3,C^2NH^2S^2) + Cl = C^2NH^2S^4 + NH^3,C^2NHS^2 + NH^4Cl.$$

2. By mixing an aqueous solution of hydrothio-sulphoprussiate of ammonia with a large excess of sulphuric or hydrochloric acid, and then immediately with a ferric salt. The reaction is precisely similar to the above, excepting that the place of the 1Cl is supplied by 1O from the ferric oxide, and instead of sal-ammoniac there is formed sulphate of oxide of ammonium, supposing the acid used to be sulphuric. The ferric salt is reduced to a ferrous salt; any ferric salt that may remain in the liquid will be reddened by the hydrosulphocyanate of ammonia.—Ferric salts likewise form these scales with hydrothio-sulphoprussiate of ammonia, potash, or baryta, without the addition of an acid; in such a case, however, their formation is preceded by that of a black precipitate. (Zeise). Hydranzothin is not formed by bringing hydropersulphocyanic acid in contact with sulphuretted hydrogen. (Völckel.)

Preparation. By adding chlorine water, with constant agitation, to a solution of hydrothio-sulphoprussiate of ammonia, till some tolerably white scales are deposited; decanting the liquid; washing the scales immediately on a filter with cold water, till the filtrate no longer reddens ferric salts; and drying them in the air, or (better) in vacuo. It is better to use too little chlorine than too much; for if too much be used the scales will be mixed with sulphur [pseudo-sulphocyanogen?] the presence of which may be recognized by the liquid not becoming clear in a short time. If the solution be too dilute, the scales take a long time to form, and remain partly dissolved. For the same reason, the washing must not be too long continued. (Zeise.) Zeise formerly prepared hydranzothin by dissolving 1 pt. of hydrothio-sulphoprussiate of ammonia in 200 pts. of water; adding, with constant stirring, a sufficient quantity of sulphuric or hydrochloric acid diluted with 18 times its weight of water, to give the liquid a strong acid reaction; then quickly, and before any deposition of sulphide of carbon could take place, adding ferric sulphate or chloride in small portions, till the liquid assumed a reddish yellow colour; and lastly, purifying the resulting scales by decantation and washing with cold water, and pressing them between paper.

Properties. White shining scales, like those of boracic acid; inodorous (after long keeping they smell slightly of sulphuretted hydrogen). Redden litmus slightly. Permanent in the air. (Zeise.)

	Crystallized.			Zeise.
2 C	12	13·04		12·30
N	14	15·22		13·63
2 H	2	2·17		2·17
4 S	64	69·57		71·74
$C^2NH^2S^4$	92	100·00		99·84

The crystals after drying in the air, lose nothing in vacuo over oil of vitriol.—According to Völckel, the compound $=C^2NHS^3,HS$, *i.e.* tersulphide of Urene with sulphuretted hydrogen (*comp.* Berzelius, *Jahresber.* 24, 98).

Decompositions. Hydranzothin heated in a retort begins to decompose at 125°; between 125° and 180°, it gives off sulphide of carbon with a small quantity of sulphuretted hydrogen, and yields a scanty white sublimate. The fused, partly brownish yellow, partly light yellow mass, gives off at a higher temperature a large quantity of hydrosulphate of ammonia, and yields a copious sublimate, consisting of hydrosulpho-carbonate of ammonia with a very small quantity of sulphur. The residue [mellon?] which is sometimes greyish brown-yellow, sometimes greyish black, sustains a strong heat without decomposing, so that a portion remains even after the retort has been raised to a red heat.—In the flame of a spirit-lamp, hydranzothin burns with a blue flame and leaves a brown-black body which does not disappear till more strongly heated.—Hydranzothin is slowly decomposed by digestion with aqua-regia, giving off a sulphuretted product.—Sulphuric and hydrochloric acid exert no perceptible action upon it.—Warm potash-ley dissolves it, forming a brownish yellow liquid which contains sulphocyanide [and sulphide] of potassium, and gives off ammonia when boiled; cold potash-ley dissolves it imperfectly. Hydranzothin likewise dissolves in alcoholic potash, forming a solution of sulphocyanide of potassium, and leaving sulphide of potassium mixed with a portion of the undecomposed substance, and apparently also with sulphur.—Similarly, hydranzothin forms with lead-oxide and water, but only when heated, sulphide of lead and crystals of sulphocyanide of lead. [In all these decompositions by metallic oxides, it is probable that a bisulphide of the metal is formed, or a mixture of the protosulphide with sulphur: *e.g.*

$$C^2NH^2S^4 + 2PbO = C^2NPbS^2 + PbS^2].$$

Hydranzothin heated with water gives off sulphide of carbon together with a small quantity of sulphuretted hydrogen and ammonia, and converts the water into an acid liquid containing hydrosulphocyanic acid together with ammonia and a small quantity of sulphuretted hydrogen; a solid body like sulphur remains undissolved.—The solution of hydrozanthin in absolute alcohol, if heated to the boiling-point and then set aside, deposits sulphur, and is converted into hydrosulphocyanic acid. (Zeise.)

Hydrozanthin dissolves very sparingly in cold water.

It dissolves without alteration in cold absolute alcohol, forming a liquid which becomes turbid when mixed with water, but does not redden ferric salts. In ether it dissolves with even greater facility, and separates out in laminæ when the liquid evaporates; the mother-liquor, however, reddens litmus strongly. It dissolves still more abundantly in acetone, and exhibits the same phenomena on evaporation. (Zeise.)

Hydropersulphocyanic Acid.

$$C^2NHS^3=C^2NHS^2,S=H,C^2NS^3=C^4N^2H^2,S^6=C^2NAd,S^3+2CS^2.$$

Wöhler. *Gilb.* 69, 271.
Liebig. *Ann. Pharm.* 43, 96.
Völckel. *Ann. Pharm.* 43, 74.—*Pogg.* 58, 138; 61, 149; 62, 150.

Sulphuretted Hydrosulphocyanic Acid, Hydroxanthic Acid, geschwefelte Schwefelblausäure, Ueberschwefelcyanwasserstoffsäure, Xanthanwasserstoff-

säure, Acide persulfocyanhydrique.—Discovered, in 1821, by Wöhler; confused for some time with pseudosulphocyanogen, till the distinction between the two compounds was pointed out by Woskresensky and Völckel.

Formed in many decompositions of hydrosulphocyanic acid and the sulphocyanides (pp. 74, 75, 83).—Thus, anhydrous hydrosulphocyanic acid decomposes spontaneously into hydrocyanic and hydropersulphocyanic acids; aqueous hydrosulphocyanic acid yields hydropersulphocyanic acid when exposed to sunshine, subjected to distillation, or acted upon by various acids, &c.;—in many decompositions of sulphocyanide of potassium by acids, &c.—In certain other decompositions of hydrosulphocyanic acid and the sulphocyanides, pseudosulphocyanogen is obtained instead of hydropersulphocyanic acid. As both these bodies form yellow powders, alcohol or ether must be used to distinguish them, only the hydropersulphocyanic acid being somewhat soluble in those liquids. (Völckel.)—Aqueous hydrosulphocyanic acid dissolves when warm a certain quantity of sulphur, which however separates out again on cooling. (Porrett.) [May not the precipitate be hydropersulphocyanic acid?]

Preparation. 1. By mixing a cold saturated aqueous solution of sulphocyanide of potassium with from 6 to 8 times its bulk of strong hydrochloric acid. The mixture at first coagulates into a white gelatinous magma, which turns yellow in a few minutes, gives off carbonic and hydrocyanic acids, after the lapse of an hour, and is converted into a mass consisting of a liquid and needles of hydropersulphocyanic acid. The needles, if collected after 24 hours and washed with cold water, constitute the pure acid. (Völckel.)—The decomposition takes place just as well with a dilute solution of sulphocyanide of potassium; but the separation of the needles is slower.—Another method is to saturate a solution of sulphocyanide of potassium in 5 parts of water, keeping it cold, with hydrochloric acid gas; the hydropersulphocyanic acid then separates after a while, on cooling, in the form of a yellow powder. If, however, the liquid be suffered to get warm from the absorption of the hydrochloric acid, part of the separated hydrosulphocyanic acid volatilizes undecomposed; the mixture likewise gives off carbonic acid gas after a while, sometimes also sulphuretted hydrogen and sulphide of carbon; and there are formed in it, hydrocyanic acid, formic acid, and ammonia, by which products the yield of hydropersulphocyanic acid is diminished, the amount of diminution being greater as the solution of sulphocyanide of potassium is more dilute, and its temperature rises higher. (Völckel.)—2. By passing dry hydrochloric acid gas over melted sulphocyanide of potassium contained in a tubulated retort, whereupon sulphide of carbon and hydrocyanic acid are evolved and hydropersulphocyanic acid sublimes. The latter is purified by dissolving it in boiling alcohol, from which it separates out again on cooling. (Liebig.)

Properties. Pale yellow, crystalline powder (Liebig), or, after crystallization from boiling water, yellow needles. The aqueous solution reddens litmus. Inodorous and tasteless. (Völckel.)

			Völckel.
2 C	12	16·00	16·18
N	14	18·67	
H	1	1·33	1·51
3 S	48	64·00	63·08
C·NHS	75	100·00	

The same composition had been previously assigned to this substance by Woskresensky. (*Liebig, Chim. org.* 1, 192.)—Hydropersulphocyanic acid may be regarded, according to Liebig and Berzelius, as a hydrogen-acid, whose radical would be a Persulphocyanogen, C^2NS^3, called by Berzelius, *Xanthan;* or, according to Völckel and Zeise (*J. pr. Chem.* 30, 301) as a compound of sulphocyanogen with sulphuretted hydrogen, C^2NS^2,HS.

Decompositions. Hydropersulphocyanic acid heated to 150°, gives off sulphuretted hydrogen and colourless sulphide of carbon, then free sulphur, at the boiling-point of that substance, and leaves a porous residue of hydromellon, C^6N^4H. (Liebig.)

At 140°, this acid gives off but a small quantity of hydrosulphocyanic acid, and remains for the most part unaltered, excepting that it becomes mixed with a certain quantity of free sulphur, which remains behind when the acid is dissolved in boiling water. Even at 145°, the amount of decomposition is but slight; a small quantity of sulphide of carbon goes off, together with the hydrosulphocyanic acid; and after the undecomposed hydropersulphocyanic acid has been dissolved out by boiling water, there remains a mixture of sulphur and *Sulphide of Melene,* $C^7N^4H^4S^6$= 4 At. hydrosulphocyanic acid − 1 At. sulphide of carbon. When the acid is kept for some time at 150°, the volatile products obtained are sulphide of carbon and hydrosulphocyanic acid, which is again resolved in the colder part of the apparatus, into hydropersulphocyanic and hydrocyanic acid; and the residue is a mixture of a large quantity of undecomposed hydropersulphocyanic acid with more or less hydrosulphocyanic acid adhering to it, *Sulphide of Xanthene,* $C^6N^4H^4S^4$, and sulphur. Boiling water dissolves out the two acids, and cold solution of potash the sulphide of xanthene, leaving the sulphur. — At 160° the decomposition is more energetic, but still incomplete even after many hours. Hydrosulphocyanic acid, hydrocyanic acid and sulphide of carbon pass over (but no sulphuretted hydrogen) and there remains a yellow mixture of hydropersulphocyanic acid (together with more or less hydrosulphocyanic acid), hydrosulphocyanate of ammonia, sulphur, a white substance soluble in water, and *Sulphide of Phaiene,* $C^8N^6H^5S^4$.—From 170° to 180°, the same products, excepting that a larger quantity of the white substance insoluble in water is produced, and that the sulphide of phaiene is accompanied by *Sulphide of Xuthene,* $C^{16}N^9H^7S^4$; a number of other products are likewise observed, some sparingly soluble in water, others readily soluble. — At 200°, similar products are obtained, sometimes accompanied by sulphuretted hydrogen. The brown, partially fused residue, after being heated for some time, no longer contains hydropersulphocyanic acid, but in addition to the above-mentioned substances, a quantity of *Sulphide of Leucene,* $C^6N^5H^5S^2$. — When hydropersulphocyanic acid is suddenly heated to 225°, and kept constantly at that temperature for some time, it likewise gives off hydrocyanic acid, hydrosulphocyanic acid, sulphide of carbon, and a small quantity of sulphuretted hydrogen; from the residue water extracts two peculiar white bodies, leaving a mixture chiefly consisting of sulphur and sulphide of leucene.—From 250° to 260°, the acid likewise evolves hydrocyanic acid, hydrosulphocyanic acid and sulphide of carbon, together with small quantities of ammonia and hydrosulphate of ammonia.—Between 290° and 300°, there remains, after all the sulphur has been driven off as sulphide of carbon, the last term of this series of decompositions, viz., *Poliene,* $C^4N^4H^4$ [$=C^8N^6H^6$.] (Völckel.) [The greater number of these fixed products, which Völckel regards as definite compounds, are probably mere mixtures.]

At 150°, hydropersulphocyanic acid is but very slightly decomposed, giving off a small quantity of hydrosulphocyanic acid and a trace of sulphuretted hydrogen; it is not till the heat rises to 200°, that these products are given off in larger quantities, together with sulphide of carbon; at 200°, the vapours, which were previously acid, begin to exhibit an ammoniacal reaction from the presence of hydrosulphate of ammonia; at a still higher temperature, crystals of hydropersulphocyanate of ammonia sublime, and sulphur distils over, accompanied by a large quantity of ammonia. If the heating be discontinued before ammonia begins to escape, the residue consists neither of mellon nor of hydromellon, but of a mixture of sulphur and poliene, from the solution of which in cold potash-ley, acetic acid throws down a gelatinous precipitate of ammelin, which is isomeric with poliene. (Laurent & Gerhardt, *Compt. rend.* 22, 457; *N. Ann. Chim. Phys.* 19, 97).

2. Dry chlorine gas does not act on hydropersulphocyanic acid at ordinary temperatures, but at a gentle heat it forms chloride of sulphur, chloride of cyanogen, and hydrochloric acid, together with a brown-red and a white substance, insoluble in water but soluble in alcohol. The brown-red body has no fixed composition. According to one analysis, it contains: 22·01 C, 25·62 N, 1·3 H, 13·51 Cl, and 37·54 S, and is therefore perhaps $C^{10}N^8H^3ClS^6$. By the further action of the chlorine, it appears to be converted into the above-mentioned volatile products. It dissolves in alcohol and in boiling potash. (Völckel).—Chlorine gas passed through aqueous hydropersulphocyanic acid gives at first a yellow precipitate, which, however, disappears if the passage of the chlorine be continued, hydrochloric and sulphuric acid being thereby produced. (Völckel.)

3. Nitric acid, especially if heated, decomposes hydropersulphocyanic acid, yielding carbonic acid, sulphuric acid, and ammonia. (Völckel.) — 4. Boiling oil of vitriol acts upon it in such a manner as to evolve sulphurous acid. (Völckel.) — 5. When hydropersulphocyanic acid is dissolved in boiling hydrochloric acid, a small portion of it is converted into carbonic acid, sulphuretted hydrogen, sulphur, and ammonia (Völckel):

$$C^2NHS^3 + 4HO = 2CO^2 + 2HS + NH^3 + S.$$

6. When hydropersulphocyanic acid is acted upon by aqueous alkalis, it appears to be resolved into sulphur and an acid intermediate in its amount of sulphur between hydrosulphocyanic and hydropersulphocyanic acid. (Völckel.)—When hydropersulphocyanic acid is dissolved in aqueous ammonia, 5 pts. of sulphur separate out in the form of white milk of sulphur. The resulting yellow solution does not appear to contain either sulphide or sulphocyanide of ammonium. When mixed with very dilute acids, it soon deposits needles of hydropersulphocyanic acid, no hydrosulphocyanic acid appearing in the solution; but when more concentrated acids are used, that acid does appear in the solution, though at the same time hydropersulphocyanic acid is precipitated. However often the precipitated hydropersulphocyanic may be redissolved in ammonia, the solution is always accompanied by the separation of 5 per cent. of sulphur. The yellow ammoniacal solution when evaporated, even in vacuo at ordinary temperatures, gradually loses its colour, and deposits hydropersulphocyanic acid as a yellow powder; and at last, nothing remains in solution but a small quautity of hydrosulphocyanate of ammonia.—When dry ammoniacal gas, which is abundantly absorbed, is passed over dry hydropersulphocyanic acid, the compound, on being

dissolved in water, deposits but a trace of sulphur, probably because the ammonia does not act in excess; but on gently heating the colourless solution, ammonia is given off and sulphur precipitated. Hence, though the greater part of the acid unites with the aqueous ammonia, without being decomposed, a small portion is nevertheless resolved into sulphur and an intermediate acid, $C^4N^2H^2O^5$; but this acid, when evaporated or precipitated by concentrated acids, is resolved into hydrosulphocyanic and precipitated hydropersulphocyanic acid. A similar action to that of ammonia is exerted by the fixed alkalis, excepting that when the solution is evaporated, the hydropersulphocyanic acid does not separate out but remains in solution. (Völckel.)

Combinations. Hydropersulphocyanic acid is but very sparingly soluble in cold water, but dissolves in boiling water, separating out again in needles as the liquid cools. (Völckel.)

It dissolves in cold oil of vitriol, and is thrown down again in its original state by water. (Völckel.)

In alcohol and in ether it dissolves more readily than in hot water.

Persulphocyanides. Such of these compounds as correspond to sulphides which are not decomposed by dilute acids, are themselves likewise undecomposible by the same means. Those which contain metals precipitable by sulphuretted hydrogen from an acid solution, are likewise, when suspended in water, completely though slowly decomposed by sulphuretted hydrogen. (Völckel, *Pogg.* 53, 135.)

Persulphocyanides of the Alkali-metals.—The solutions of hydropersulphocyanic acid in aqueous alkalis must be regarded as of this nature, although they likewise contain sulphocyanides. The solutions precipitate the salts of the heavy metals in the same manner as the aqueous acid. (Völckel.)

Lead-salt. a. *Neutral.*—A boiling aqueous solution of hydropersulphocyanic acid forms with acetate of lead a bright yellow precipitate. If an alcoholic solution be used, the alcohol robs the precipitate of part of its acid, so that the following basic salt is formed.—The salt gives off a certain quantity of sulphide of carbon even at 100°, and without losing water: at a higher temperature, it gives off a large quantity of sulphide of carbon, together with small quantities of hydrosulphocyanic acid and sulphur, then cyanogen, and leaves sulphide of lead. It does not dissolve in water, in dilute acids, or in alcohol. (Völckel.)

b. *Basic.*—Formed by precipitating the aqueous solution with excess of basic acetate of lead. The precipitate resembles the preceding, and is converted into it by acids. It yields the same products by dry distillation. (Völckel.)

(*a*). *Dried at* 100°.			Völckel.	(*b*). *Dried at* 100°.			Völckel.
2 C	12	6·74	6·48	4 C	24	5·13	5·15
N	14	7·87		2 N	28	5·98	6·01
Pb	104	58·42	58·67	3 Pb	312	66·67	66·93
3 S	48	26·97		6 S	96	20·51	
H			0·23	O	8	1·71	0·22
C^2NPbS^3	178	100·00		$2C^2NPbS^3,PbO$	468	100·00	

The aqueous acid forms yellow precipitates with protochloride of *tin* and sulphate of *copper;* with nitrate of *silver* it yields a yellow preci-

pitate which easily decomposes, with formation of sulphide of silver, and with bichloride of *platinum* a brownish yellow precipitate. The salts of the other heavy metals are not precipitated by it. (Völckel.)

Pseudosulphocyanogen.

Wöhler. *Gilb.* 69, 271.
Liebig. *Pogg.* 15, 548. *Ann. Pharm.* 10, 1; also *Pogg.* 34, 571.—*Ann. Pharm.* 11, 12; 25, 4.—*Ann. Pharm.* 39, 109, 201 and 202 (die Anmerkungen).—*Ann. Pharm.* 50, 337.
Parnell. *Phil. Mag. J.* 17, 249; also *Ann. Pharm.* 39, 198.
Völckel. *Ann. Pharm.* 43, 80.—*Pogg.* 58, 145; 62, 607.
Laurent & Gerhardt. *N. Ann. Chim. Phys.* 19, 98; also *Compt. rend.* 22, 460.
Alex. Jamieson. *Ann. Pharm.* 59, 339.

The so-called *Sulphocyanogen* (Liebig), *Oxysulphide of Cyanogen* (Völckel).—This compound was first obtained by Wöhler, who regarded it as identical with hydropersulphocyanic acid, C^2NHS^3, which he discovered at the same time. Liebig afterwards pronounced it to be sulphocyanogen, C^2NS^2, or a compound isomeric therewith; the more recent analyses by Parnell, Völckel, Laurent & Gerhardt, and Jamieson, have assigned to it a more complicated formula, but even this is not yet completely determined.

Formation. By the action of chlorine and oxidizing agents on hydrosulphocyanic acid and the aqueous solutions of the sulphocyanides.

Preparation. 1. By heating nitric acid with sulphocyanide of potassium.—Wöhler boils sulphocyanide of potassium with dilute nitric acid, till a sufficient quantity of pseudosulphocyanogen is separated, and collects the product immediately on a filter, because it would be decomposed by longer boiling.—Liebig dissolves 1 pt. of sulphocyanide of potassium in a mixture of 2 to 2½ pts. strong nitric acid of sp. gr. 1·43, and 3 pts. water, decants the mixture from the crystals of nitre which are produced, and heats it gently, till it suddenly boils up violently, giving off nitric oxide and carbonic acid, and depositing pseudosulphocyanogen, which is then collected in a filter. If more than 3 pts. of nitric acid be used, the process fails altogether.

2. By passing chlorine gas through an aqueous solution of sulphocyanide of potassium.—Liebig uses a concentrated solution of the sulphocyanide (which must be free from carbonate of potash, or if it contains that compound, must be purified from it by means of hydrochloric acid), and warms it, to prevent the stoppage of the gas-delivery tube by the crystallization of chloride of potassium. The more concentrated the solution, the more does the yellow colour of the precipitate incline to reddish; if the solution be too dilute, no precipitate is obtained.—Völckel, on the contrary, cools the concentrated solution of sulphocyanide of potassium with cold water, while the chlorine is being passed into it.—From a moderately dilute solution, a lighter coloured precipitate of hydrothiocyanic acid is obtained in place of the pseudosulphocyanogen. *(Parnell.)*

Pseudosulphocyanogen is best purified by solution in oil of vitriol and precipitation by water.

The pseudosulphocyanogen produced by nitric acid is contaminated with hydrothiocyanic acid; on treating the product with aqueous potash, the pseudosulphocyanogen dissolves first, and the residue, consisting chiefly of hydrothiocyanic acid, exhibits a paler yellow colour. (Parnell.)

Properties. Orange-yellow, amorphous powder, or loosely aggregated mass, soft to the touch, producing a strong stain, and inodorous. (Wöhler, Liebig.)—The yellow powder prepared by (2) frequently appears under the microscope to be mixed with white [pale yellow ?] needles and scales [of hydropersulphocyanic or hydrothiocyanic acid?]; if however the passage of the chlorine be interrupted now and then, and the liquid filtered, some of the precipitates obtained appear almost free from crystals. (Laurent and Gerhardt.)

Calculation of the composition, according to various formulæ.

Liebig. (*earlier.*)			Parnell.			Völckel.		
2 C....	12	20·69	12 C....	72	20·06	8 C....	48	19·83
1 N....	14	24·14	6 N....	84	23·40	4 N....	56	23·14
2 S....	32	55·17	12 S....	192	53·48	8 S....	128	52·89
			3 H....	3	0·83	2 H....	2	0·83
			O....	8	2·23	O....	8	3·31
	58	100·00		359	100·00		242	100·00

Laur. & Gerh.			Jamieson.		
6 C	36	20·57	4 C	24	19·04
3 N	42	24·00	2 N	28	22·22
6 S	96	54·86	4 S	64	50·80
H	1	0·57	2 H	2	1·58
			O	8	6·36
	175	100·00		126	100·00

Analyses:

	Liebig.	Parnell.	Völckel.	Laur. & Gerh.	Jamieson.
C		20·06	19·93	20·45	19·17
N		23·23	23·31		22·36
S	55·84 to 56·15	52·59	52·68	53·90	50·88
H	0·33 to 0·96	0·92	1·08	0·66	1·58
O		3·20	3·00		6·01
		100·00	100·00		100·00

All these analyses were made with pseudosulphocyanogen obtained by the action of chlorine on aqueous sulphocyanide of potassium.—Liebig dried it in vacuo before analysing it.—Parnell dried it partly over the water-bath, partly at 242°, at which latter temperature a slight odour of cyanogen was apparent.—Völckel does not state the temperature at which his substance was dried.—Laurent & Gerhardt dried the portion which appeared under the microscope to be nearly free from white crystals, for a long time, and at a high temperature. Jamieson boiled the precipitate with water as long as anything was dissolved out, and examined the pure yellow powder which remained. During this boiling, the odour of cyanogen was perceptible, and the water dissolved hydrosulphocyanic acid, together with a small quantity of another sulphur-compound. As the preparation might have been decomposed during this long boiling,

and moreover it is not stated how the substance was dried before analysis, the analytical results are not much to be trusted, especially as the amount of oxygen comes out too great. This amount of oxygen is regarded by Liebig (*Ann. Pharm.* 50, 337) as very problematical, inasmuch as, in the dry distillation of pseudosulphocyanogen, no oxygenized product is obtained, except water; Liebig however regards the considerable amount of hydrogen obtained by Jamieson as very probable.

Decompositions. Pseudosulphocyanogen heated in a glass tube gives off cyanogen gas, sulphur, and sulphide of carbon, and leaves a yellow body [mellon], which disappears without residue at a red heat. (Liebig.) It gives off sulphur, sulphide of carbon, hydrosulphocyanic acid, and ammonia, and leaves mellon. (Völckel, *Ann. Pharm.* 43, 88.) [What becomes of the oxygen which Völckel supposes to exist in pseudosulphocyanogen?] It gives off nothing but sulphur and sulphide of carbon, and leaves mellon. (Laurent and Gerhardt.)

$$3C^6N^3HS^6 = S + 6CS^2 + C^{12}N^9H^3.$$

If the pseudosulphocyanogen is moist, it gives off, when heated, sulphur and carbonate of ammonia, and leaves a black residue, which burns away in the air with a glimmering light. (Liebig.)

2. Dry chlorine gas does not act on slightly heated pseudosulphocyanogen; at a somewhat higher temperature, it abstracts the greater part of the hydrogen, so that the residue, when subjected to dry distillation, gives off mere traces of hydrosulphocyanic acid; at a red heat, the chlorine gives off chloride of sulphur, fixed chloride of cyanogen, and a yellow residue [mellon]. (Liebig, *Pogg.* 15, 559, and *Ann. Pharm.* 39, 212.) At ordinary temperatures, the chlorine exerts no action; at 100° it acts feebly; at 200° it produces chloride of sulphur, hydrochloric acid, fixed chloride of cyanogen, and a yellow residue of mellon. (Völckel, *Pogg.* 58, 145.) — 3. Nitric acid decomposes pseudosulphocyanogen, with formation of sulphuric acid. (Wöhler.)

4. Pseudosulphocyanogen heated in the perfectly dry state with potassium, exhibits vivid incandescence, gives off a combustible gas, and leaves a yellow mixture of sulphocyanide and sulphide of potassium. (Wöhler.) The combustible gas is perhaps cyanogen, mixed with the vapours of sulphur and sulphide of carbon; the fused yellow mixture turns red when kept for some time in the fused state; after fusion for a short time, it often contains nothing but sulphocyanide and cyanide of potassium; after longer fusion, also sulphide of potassium.

5. Pseudosulphocyanogen dissolves readily in aqueous hydrosulphate of potassium, forming hydrosulphocyanic and hydrothiomellonic acid, the latter being separated on the addition of a stronger acid, in the form of a yellowish white mucus. (Liebig, Jamieson.)—The solution of pseudosulphocyanogen in aqueous protosulphide of potassium, after precipitation by hydrochloric acid and filtering, imparts a dark red colour to ferric salts. Similarly with the solution in sulphide of barium; if the pseudosulphocyanogen is in excess, the filtered solution does not actually blacken lead-salts; but when treated with acids, it gives off sulphuretted hydrogen; and the liquid filtered from the yellowish white precipitate, forms with ferric salts a deep red mixture, which is clear at first, but after a while deposits a yellowish precipitate. (Liebig, *Pogg.* 15, 556.)—The solution of pseudosulphocyanogen in aqueous hydrosulphate of potassium yields with hydrochloric acid a yellowish white, gummy precipitate, the amount

of sulphur in which differs considerably from that in pseudosulphocyanogen; mellonide of potassium and sulphocarbonate of potassium KS,CS^2, appear to be formed in this reaction. (Liebig, *Ann. Pharm.* 39, 112.)—When pseudosulphocyanogen is dissolved in hydrosulphate of potassium, a small quantity of a brown substance remains undissolved. The yellowish white gummy precipitate produced by acids is hydrothiomellonic acid, $C^6N^4H^4S^4$, its formation being represented by the following equation [in which, however, pseudosulphocyanogen is incorrectly regarded as C^2NS^2]:

$$4C^2NS^2 + 4(KS,HS) + 6HO = \underbrace{C^6N^4H^3KS^4}_{\text{Sulphomellonide of potassium.}} + 7HS + KS^5 + 2(KO,CO^2).$$

Hence the acid precipitated from this solution by hydrochloric or acetic acid is contaminated with sulphur derived from the KS^5. Gerhardt gives the following equation, in which pseudosulphocyanogen is regarded as $C^6H^3HS^6$:

$$2C^6N^3HS^6 + 4HO = C^6N^4H^4S^4 + \underbrace{2C^2NHS^2}_{\text{Hydrosulphocyanic acid.}} + 2CO^2 + 4S.$$

According to Jamieson's own statement, the solution contains a large quantity of sulphocyanide of potassium.

6. With cold aqueous solutions of the alkalis, pseudosulphocyanogen appears to unite without decomposition (*vid. inf.*); but on the application of heat, a solution is formed, which, instead of pseudosulphocyanogen, contains hydrothiocyanic acid, hydrosulphocyanic acid, and other products. Pseudosulphocyanogen boiled with caustic potash acquires a deeper yellow colour, without dissolving; after decantation of the alkaline liquid, it dissolves in water, leaving however a yellow substance, and for the most part also in alcohol, forming a solution which imparts a dark red colour to ferric salts. (Liebig, *Pogg.* 15, 555.)—The dark red solution of pseudosulphocyanogen in potash becomes light yellow and gives off ammonia when boiled with potash for a longer time; if it be then mixed with acids, it effervesces briskly, and yields a precipitate consisting of sulphur, and a pale yellow substance, which separates on cooling from a solution in boiling water, in pale yellow flakes. (Liebig, *Ann. Pharm.* 50, 337.)—3 pts. of pseudosulphocyanogen dissolve in a solution of 4 pts. hydrate of potash in 25 pts. water, partially in the cold, completely when the liquid is heated, the solution exhibiting at first a yellowish red colour. The reddish-yellow liquid deposits, on cooling, a brown-black substance, like paracyanogen, insoluble in water and alcohol. From the remaining liquid, acids throw down a yellow mixture of a similar brown-black substance and hydrothiocyanic acid, which latter may be partially dissolved out by boiling alcohol, and then completely by potash. Besides hydrothiocyanic acid and the brown-black substance, the alkaline solution also contains sulphocyanide of potassium and a small quantity of sulphite of potash. (Parnell.)—If the potash-solution be allowed to act on excess of pseudosulphocyanogen, the precipitate thrown down by acids from the resulting solution likewise contains undecomposed pseudosulphocyanogen, which may be separated by its greater solubility; if, on the other hand, the potash-ley is in excess, or if the mixture be heated for a longer time, the precipitate thrown down by acids is of a paler yellow colour and looser consistence. Hydrothiocyanic acid is also produced

when pseudosulphocyanogen is boiled with baryta-water or carbonate of potash. On heating it with aqueous ammonia, the liquid takes up a small quantity of sulphate of ammonia and a trace of hydrothiocyanate, and the undissolved yellow body which constitutes the principal portion is free hydrothiocyanic acid. (Parnell.)—When pseudosulphocyanogen is continuously boiled with dilute potash, and the solution precipitated by acids, sulphuretted hydrogen and hydrosulphocyanic acid are set free, and the resulting precipitate, when boiled with alcohol, leaves not a brown-black, but a yellowish white residue. (Völckel, *Ann. Pharm.* 43, 89, and *Pogg.* 58, 145.)

Combinations. Pseudosulphocyanogen is insoluble in water.

It dissolves in oil of vitriol, and is precipitated from the solution in its original state by water. (Wöhler, Liebig.)

It dissolves sparingly in alcohol (Wöhler); is insoluble both in alcohol and in ether. (Völckel). That which Wöhler found to dissolve in alcohol was probably an admixture of hydropersulphocyanic acid.

Salts of Pseudosulphocyanogen.—If it may be assumed that the alkalis in the state of aqueous solution unite at ordinary temperatures with pseudosulphocyanogen, without producing any alteration in it, the following compounds must be enumerated under this head.

Ammonia-salt.—Cold aqueous ammonia dissolves but a small quantity of pseudosulphocyanogen (the greater part according to Liebig); the solution gives off all its ammonia when evaporated. (Wöhler.)

Potash-salt.—Pseudosulphocyanogen immersed in solution of potash acquires a deeper orange-yellow colour without dissolving to any considerable amount; on decanting the yellow alkaline liquid, washing the residue with alcohol, and pouring water upon it, it immediately acquires a ruby colour and dissolves quickly. The reddish yellow neutral liquid leaves on evaporation a red, transparent, brittle mass, which dissolves easily in water, sparingly in potash, and, when heated, gives off sulphur and fuses into pure colourless sulphocyanide of potassium. (Wöhler.) Pseudosulphocyanogen triturated with cold concentrated potash-solution, dissolves completely on the addition of a large quantity of water. Hydrochloric acid added to the solution throws down the pseudosulphocyanogen in its original state, and the supernatant liquid does not retain any compound of sulphocyanogen. (Völckel.)

Lead-salt.—The solution of the potash-salt forms a yellow precipitate with lead-salts. (Wöhler.) If the solution obtained by triturating pseudosulphocyanogen with strong potash-ley and adding a large quantity of water, be precipitated with excess of acetate of lead, and acetic acid added till an acid reaction is produced a yellowish brown precipitate is obtained, the composition of which is as follows:

			Völckel.
8 C	48	10·71	10·55
4 N	56	12·50	
2 Pb	208	46·43	46·09
8 S	128	28·57	
O	8	1·79	
	448	100·00	

The aqueous solution of the potash-salt does not redden ferric salts; it forms yellow precipitates with *cupric salts* and with *mercurous* nitrate, and a deep yellow with nitrate of *silver*. (Wöhler.)

Lassaigne's Sulphocyanogen?

When 1 pt. of protochloride of sulphur and 2 pts. cyanide of mercury are sealed up in a wide glass tube, and left for several days at a temperature of 15° to 20°, protochloride of mercury remains at the bottom of the tube, together with an orange-yellow substance not yet examined, while a sublimate is formed, amounting to $\frac{1}{25}$ of the whole, and consisting of transparent and colourless rhombic laminæ, having a pungent odour like that of chloride of cyanogen, and a caustic taste. These crystals contain 24·2 p. c. sulphur, and 75·8 p. c. cyanogen, and therefore consist of SCy^2? [The quantity of cyanogen was not determined directly, and no search whatever was made for chlorine.] The laminæ generally assume a yellow and afterwards an orange colour. Potassium decomposes them with evolution of heat, and sometimes with visible combustion, forming sulphide and cyanide of potassium. They dissolve in aqueous potash, forming sulphocyanide of potassium. They dissolve more readily in water, less readily in alcohol; the former solution reddens litmus strongly, the latter only on addition of water. The aqueous solution converts finely divided silver into sulphide. (Lassaigne, *Ann. Chim. Phys.* 39, 197; also *J. Chim. méd.* 5, 1; also *Schw.* 55, 132.)

Liebig (*Pogg.* 15, 559), using dry materials, obtained no crystalline sublimate, even after several months; in presence of a small quantity of water, the mixture gave off pure cyanogen gas on the application of a gentle heat, and with more water a large quantity of sulphurous acid gas was likewise evolved, but no crystals sublimed.

Hydrothiocyanic Acid. $C^{10}N^{5}H^{6}S^{12}O^{2}$.

Hydrothiocyansäure, Thiocyanwasserstoffsäure.—Discovered by Parnell in 1840.

Formed by the action of aqueous alkalis on pseudosulphocyanogen. Also, when chlorine gas is passed through a sufficiently dilute solution of sulphocyanide of potassium, this lighter yellow acid is precipitated instead of pseudosulphocyanogen. (Parnell.)

Preparation. 3 parts of pseudosulphocyanogen are digested for three hours at 49° with a solution of 4 pts. hydrate of potash in 25 pts. water; the liquid then boiled for half an hour; the solution filtered from the brown-black substance which separates on cooling; hydrochloric acid added; the resulting precipitate washed on a filter with cold water till the chloride of potassium is removed; the residue boiled with alcohol; the solution filtered from the residual brown matter; and the filtrate distilled nearly to dryness. (Parnell.)

The acid remains in the residue in pale, lemon-yellow, crystalline flakes. It tastes, after a while, extremely bitter and sharp; introduced into the nose in the form of dust, it excites sneezing; its aqueous solution reddens litmus after a while. (Parnell.)

The quantity of acid obtained by continued boiling of pseudosulphocyanogen with dilute potash, precipitating with hydrochloric acid, and

exhausting the precipitate with boiling alcohol, which leaves a yellowish white residue, is but small; by continued boiling with potash it suffers further decomposition, sulphocyanide of potassium being formed; it requires 500 pts. of alcohol to dissolve it completely; its composition appears also to be different from that which Parnell assigns to it (*vid. inf.*). The acid appears therefore to differ in composition according to the process by which it is obtained. (Völckel.)

	At 100°.			Parnell.	Völckel.
10 C	60	17·44		17·59	16·77
5 N	70	20·35		20·37	19·71
6 H	6	1·75		1·76	1·78
12 S	192	55·91		55·16	58·76
2 O	16	4·65		3·12	2·98
$C^{10}N^5H^6S^{12}O^2$	344	100·00		100·00	100·00

According to Parnell, it is $2HO.C^{10}N^5H^6S^{12}$, but he likewise regards it as a quadrobasic acid.

The acid heated in a tube gives off sulphur, sulphide of carbon, and sulphuretted hydrogen, and leaves a brown substance [mellon?]. In the air it burns with a sulphureous flame, leaving the same brown substance. —By nitric acid it is completely converted into sulphuric and carbonic acid, with evolution of nitrous fumes.

It is scarcely soluble in cold water, but dissolves in 42 pts. of boiling water.

It dissolves in oil of vitriol, and is precipitated by water without alteration. It is likewise slightly soluble in hydrochloric acid.

It dissolves in 25 parts of cold and 7 pts. of boiling alcohol; the yellow solution, if concentrated, is precipitated by water; when evaporated, it becomes covered with a shining film, but yields no crystals.—*Wood-spirit* exhibits about the same degree of solvent power, likewise forming a yellow solution which is precipitated by water.

The acid decomposes the alkaline carbonates only at a boiling heat. Its salts, the *Thiocyanides*, are not crystallizable; those of the alkalis are yellow; those of the heavy metals white, yellow, brown, or black. The alkaline thiocyanides are partially decomposed by boiling their aqueous solutions.

Ammonia-salt.—The solution obtained by digesting the acid in aqueous ammonia yields, by evaporation in vacuo in the neighbourhood of a free acid, a yellow, neutral, very bitter salt, soluble in water.

Potash and Soda-salts.—The solution of the acid in either of these alkalis leaves on evaporation a yellow amorphous residue.

Baryta-salt.—By digesting baryta water with the acid, precipitating the excess of baryta by carbonic acid gas, filtering, and evaporating the yellow filtrate, a yellow amorphous residue is obtained.

Tin-salt.—The aqueous acid forms a yellow precipitate with hydrochlorate of stannic oxide.

Lead-salt.—Formed by precipitating either the neutral or the basic acetate of lead with the aqueous acid. The yellow precipitate subjected to dry distillation yields sulphur, sulphide of carbon, cyanic acid, and sulphide of lead. With nitric acid it immediately yields sulphate of lead.

Others of the stronger acids, as well as hydrosulphuric acid, precipitate the hydrothiocyanic acid from it without alteration. Aqueous alkalis blacken it by forming a basic salt.

Calculation (*a*).			Calculation (*b*).			Parnell.
10 C	60	7·75	6 C	36	9·02	8·67
5 N	70	9·04	3 N	42	10·53	
4 H	4	0·52	H	1	0·25	0·50
4 Pb	416	53·75	2 Pb	208	52·13	51·95
12 S	192	24·81	6 S	96	24·06	
4 O	32	4·13	2 O	16	4·01	
	774	100·00		399	100·00	

[Calculation *a* is made according to Parnell's hypothesis; calculation *b*, which agrees better with the analysis, is based on the supposition that hydrothiocyanic acid is $C^6N^3H^3S^6O^2$. If pseudosulphocyanogen be really $C^6N^3HS^6$, as supposed by Laurent & Gerhardt, hydrothiocyanic acid must, according to the latter formula, be *Pseudosulphocyanogen* + 2HO. But the calculation of the acid itself according to this formula does not agree well with Parnell's analysis. Either the acid examined by Parnell or its lead-salt was impure; for it is impossible to devise a formula in accordance with both.]

Copper-salt.—The aqueous acid forms an ochre-brown precipitate with sulphate of copper. The dried precipitate is resolved by destructive distillation into sulphur, sulphide of carbon, cyanic acid, and sulphide of copper. Nitric acid, oil of vitriol, hydrochloric acid, and hydrosulphuric acid decompose it, and alkalis convert it into a black basic salt.

Mercury-salt.—The aqueous acid forms a black precipitate with mercurous nitrate, but with corrosive sublimate a white precipitate which turns yellow when the liquid is heated. This precipitate, when dry, yields by destructive distillation the same products as the lead-salt; nitric acid converts it into a white powder, which dissolves immediately on the addition of hydrochloric acid; alkalis convert it into a basic salt.

Silver-salt.—The solution of 1 pt. acid in 10,000 pts. water is still in a condition to precipitate nitrate of silver. The yellow flakes obtained by using more concentrated solutions slowly collect together, turning black at the same time, but without giving off gas, the change being accelerated by sunshine or by heat. On adding a small quantity of silver-solution to an aqueous mixture of hydrothiocyanic and hydrochloric acids, hydrothiocyanate of silver is first precipitated, and afterwards, on the addition of more silver-solution, the chloride of silver.—The black precipitate contains 70·14 p. c. silver and 16·01 p. c. sulphur; hence it appears to be a compound of the neutral silver-salt with oxide of silver. —Boiling hydrochloric acid decomposes the precipitate, giving off sulphuretted hydrogen. Nitric acid dissolves and decomposes it at the same time; oil of vitriol exerts no action upon it; dilute sulphuric acid and sulphuretted hydrogen separate the hydrothiocyanic acid, and form sulphate or sulphide of silver. The salt is insoluble in ammonia.

Platinum-salt.—The aqueous acid forms a yellow precipitate with bichloride of platinum. (Parnell.)

Sesqui-hydrosulphate of Cyanogen. $2C^2N,3HS$?

Literature for Sesqui-hydrosulphate and Bi-hydrosulphate of Cyanogen.

GAY-LUSSAC. *Ann. Chim.* 95, 136; also *Gilb.* 53, 163; also *Schw.* 16, 51.
VAUQUELIN. *Ann. Chim. Phys.* 9, 113; also *Schw.* 25, 71.
PORRETT. *Ann. Phil.* 13, 363.
WÖHLER. *Gilb.* 69, 276,—*Pogg.* 3, 177.
LIEBIG & WÖHLER. *Pogg.* 24, 167.
VÖLCKEL. *Ann. Pharm.* 38, 314,—*Pogg.* 62, 115; 63, 96.
LAURENT. *Laur. & Gerh. C. R.* 1850, 373; *Pharm. Centr.* 1851, 93; abstr. *Compt. rend.* 30, 618; *Instit.* 1850, 162; *Jahresber.* 1850, 360.

Flaveanswasserstoffsäure (Berzelius), *Unterschwefeluren-Schwefelwasserstoffsäure* (Völckel).—Discovered in 1815 by Gay-Lussac; more minutely examined by Vauquelin, Porrett, and Völckel. ¶ More recently by Laurent, who assigns to it the formula $C^4H^2N^2S^2$, or C^2HSN, and regards it as a kind of amide of oxalic acid, to which he gives the name of *Sulphoxalenide* (*oxalénide sulfuré.*) ¶.

Formation. A mixture of cyanogen gas and sulphuretted hydrogen, the latter not in excess, condenses slowly in the proportion of 2 vol. cyanogen to 3 vol. sulphuretted hydrogen, forming yellow needles. (Gay-Lussac.) In the dry state the gases do not act upon one another. (Porrett, Vauquelin.) But a drop of water quickly gives rise to the formation of greenish yellow crystals—or brownish yellow if the cyanogen is in excess—only partially soluble in water. The aqueous solutions of the two gases, however, act upon one another in the same manner. (Porrett.) [The excess of cyanogen probably forms with the water a substance of the nature of paracyanogen]. If a larger quantity of water be admitted to the gases, they condense immediately, forming an aqueous solution of the needles. (Vauquelin.)

Preparation. 2 vol. cyanogen gas are mixed in a bell-jar over mercury with not more than 3 vol. sulphuretted hydrogen, in the undried state. (Gay-Lussac.) — 2. The two gases are passed together, the cyanogen being a little in excess, into [absolute?] alcohol. The alcohol acquires a yellow colour, and on evaporation leaves the compound crystallized in radiated groups. If too much sulphuretted hydrogen be present, the alcohol deposits the red compound, or a mixture of the two, instead of the yellow. Water may also be used instead of alcohol; but in that case part of the yellow compound is decomposed, with deposition of a brown substance. (Völckel.) [Although Völckel states (*Ann. Pharm.* 38, 314,) that the alcoholic solution, when evaporated, yields the pure compound in crystals, he nevertheless remarks (*Ann. Pharm.* 38, 319,) that when the alcohol is evaporated, either at ordinary, or at higher temperatures, it is almost wholly decomposed, and converted into a brown substance containing sulphur, and consequently is not likely to be obtained in the pure state by this process.] — ¶ 3. Laurent passed cyanogen and sulphuretted hydrogen (the latter in great excess) into a large bottle, the sides of which were moistened with water, and purified the resulting yellow needles by recrystallization from ether. ¶

Properties. Yellow needles. (Gay Lussac.) The aqueous solution does not redden litmus; it is inodorous, but has a very pungent taste, and strongly bitter after-taste. (Vauquelin.)

Calculation. According to Gay-Lussac.			According to Laurent.			*Analysis.* Laurent.
4 C	24	23·30	2 C	12	27·9	26·0
2 N	28	27·19	N	14	32·6	
3 H	3	2·91	H	1	2·3	2·3
3 S	48	46·60	S	16	37·2	38·2
$C^4N^2H^3S^3$	103	100·00	C^2NHS	43	100·0	

As the presence of water is essential to the formation of this compound, it is possible that the constituents of the water may enter into it; in which case the compound will be $C^4N^2H^4S^3O$.—Berzelius regards it as the hydrogen-acid of an unknown radical, *Flavean*, $C^4N^2H^2S^3$, and therefore represents it by the formula $H,C^4N^2H^2S^3$.—Völckel regards it as a compound of 2 At. sulphide of urene, C^2NHS, with 1 At. hydrosulphuric acid, $= 2C^2NHS,HS$; he likewise remarks that it may be considered as allantoin, $C^4N^2H^5O^3$, in which 3O are replaced by 3S.—¶. According to Laurent's analysis, this compound is not a sesqui- but a proto-hydrosulphate of cyanogen, C^2N,HS. As, however, it is converted by acids and alkalis in presence of water into oxalic acid and ammonia (in a similar manner to the following compound, *q.v.*), Laurent regards it as a kind of amide of oxalic acid, viz. as *Sulphoxalenide* (*oxalénide sulfuré*), the sulphur-compound corresponding to *oxalenide* (oxalate of ammonia *minus* 3 At. water), a compound not yet actually obtained: thus, Oxalenide $= (C^2HO^4,NH^4—3HO) = C^2HNO$; Sulphoxalenide $= C^2HNS$. ¶.

Decompositions. The aqueous solution kept out of contact of air, assumes a brown colour of continually increasing intensity, acquires the odour of hydrocyanic acid, and, like an aqueous solution of cyanogen, deposits brown flocks. (Vauquelin.) The alcoholic solution, when evaporated, undergoes a similar decomposition, depositing a brown substance containing sulphur. (Völckel.)—The compound, when boiled with dilute acids or alkalis, takes up 6 At. water, and is resolved into hydrosulphuric acid, ammonia, and an oxalate of the alkali; but, when boiled with a strong solution of potash, it takes up 3 At. water, and forms sulphide, cyanide, and sulphocyanide of potassium. (Völckel.)

$$C^4N^2H^3S^3 + 2KO + 6HO = C^4K^2O^8 + 2NH^3 + 3HS.$$

and

$$C^4N^2H^3S^3 + 3KO = KS + C^2NK + C^2N^2KS^2 + 3HO.$$

The aqueous solution throws down sulphide of silver from the nitrate, with evolution of cyanogen (Vauquelin, Völckel):

$$C^4N^2H^3S^3 + 3(AgO,NO^5) = 2C^2N + 3AgS + 3HO + 3NO^5.$$

On mixing the aqueous solution, first with potash, and then with an acid, the formation of hydrosulphocyanic acid becomes apparent. (Porrett.)—The aqueous solution does not form an immediate precipitate with nitrate of lead, (Gay-Lussac,) or with the neutral acetate, (Vauquelin) or terbasic acetate of lead (Völckel); but with the neutral acetate, sulphide of lead is precipitated after some time (Vauquelin, Völckel); and, even if the mixture be supersaturated with potash, a yellow precipitate is formed which soon turns black. (Vauquelin.)—The clear mixture of the aqueous acid with green vitriol, if precipitated by

potash, and then supersaturated with hydrochloric acid, yields a small quantity of prussian blue. (Vauquelin.)

Combinations. Soluble in water and alcohol.

The aqueous solution forms grey or brown precipitates with the salts of mercury, gold, and palladium. (Porrett.)—The solution of chloride of gold yields a brown precipitate, without evolution of cyanogen. (Vauquelin.)—The brownish yellow precipitate, formed with acetate of copper, decomposes very quickly. (Völckel.)

Bi-hydrosulphate of Cyanogen. $C^2N,2HS$.

For the Literature, vid. Sesqui-hydrosulphate of Cyanogen (p. 116).

Hydrorubeanic acid, Rubeanwasserstoffsäure (Berzelius); *Schwefeluren-Schwefelwasserstoffsäure* (Völckel). — Obtained by Gay-Lussac in the form of a baryta-compound; prepared in the separate state by Wöhler in 1821, and more exactly investigated both by him and by Liebig and Völckel.

Formation and Preparation. 1. When alcohol is saturated, first with cyanogen gas, and then with sulphuretted hydrogen, it acquires a deep yellow colour, and deposits a large number of small crystals of this compound. (Wöhler.) The two gases may also be passed into the solution simultaneously, the sulphuretted hydrogen, however, being kept in excess. During this process, the alcohol first turns yellow in consequence of the formation of sesqui-hydrosulphate of cyanogen, but afterwards yellowish red, the sesqui-hydrosulphate being, by the further action of the sulphuretted hydrogen, gradually converted into bihydrosulphate; to render the conversion complete, the passage of the sulphuretted hydrogen must be continued for a considerable time. The crystals must be recrystallized from alcohol to purify them from obstinately adhering traces of mercaptan and sulphide of ethyl. (Völckel).

2. Also when the two gases are brought together in a vessel containing water, and their absorption is promoted by agitation, the water soon acquires a yellow colour, and deposits a continually increasing quantity of bihydrosulphate of cyanogen in yellow crystalline flocks, which, by filtration and washing with cold water, may be separated from the yellow compound which always forms at the same time, but remains in solution : the red compound may be obtained in the crystalline form by dissolving it in hot alcohol and cooling the solution. (Wöhler.) In this process, the passage of the sulphuretted hydrogen must be continued for a much longer time, to convert the yellow compound completely into the red. The crystals which it yields are always contaminated with a brown substance, resulting from the decomposition of the yellow compound formed at the commencement ; hence the solution of the crystals in hot alcohol must be purified by digestion with animal charcoal and crystallizing. (Völckel.)

3. When cyanogen gas is passed through an aqueous solution of hydrosulphate of barium, sulphur is at first precipitated, but if the passage of the gas be continued, the precipitate dissolves, and a dark brown liquid is formed. (Gay-Lussac.) On adding an acid, acetic acid for example, to this solution, a copious precipitate is formed consisting of the red compound. (Wöhler.) Similarly, an aqueous solution of monosulphide or persulphide of ammonium absorbs a considerable quantity of cyanogen,

and deposits a portion of the compound, first of a light orange-yellow, but afterwards of a darker colour; the remainder may be precipitated by acetic acid. (Wöhler.)

Properties. Small, yellowish red, shining, opaque crystals.

			Völckel.					Liebig & Wöhler.
2 C	12	20·00	20·15	6 C	36	19·06	41·11	
N	14	23·33		3 N	42	22·22		
2 H	2	3·33	3·46	7 H	7	3·70	3·54	
2 S	32	53·34	53·32	6 S	96	50·79	50·04	
				O	8	4·23	5·31	
$C^2NH^2S^2$	60	100·00		$3C^2NH^2S^2,HO$	189	100·00	100·00	

Berzelius regards the compound as the hydrogen-acid of a peculiar hypothetical radical, *Rubean*, C^2NHS^3, therefore $= H,C^2NHS^2$; Völckel regards it as a compound of 1 At. sulphide of urene with 1 At. hydrosulphuric acid $= C^2NHS,HS$.—Laurent (*Compt. rend.* 20, 850 : *N. Ann. Chim. Phys.* 18, 280) views it, as Völckel did formerly (*Ann. Pharm.* 38, 318), as oxamide, $C^2N^2H^4O^4$, in which the oxygen is replaced by sulphur, and calls it *Sulphoxamide (oxamide sulfuré)*, inasmuch as both these compounds, when treated with alkalis, yield oxalic acid.

Decompositions. 1. When this compound is gently heated, the smaller portion of it sublimes undecomposed, while the greater part turns black, gives off hydrosulphate of ammonia, and leaves charcoal (Wöhler). Heated with finely-divided copper, it gives off a large quantity of ammoniacal gas (Wöhler) and water (Liebig and Wöhler.) — 2. Chlorine gas decomposes the compound when heated, and forms chloride of sulphur. (Völckel.). — 3. Nitric acid heated with the compound, forms sulphuric acid. (Wöhler). — 4. The compound, boiled with aqueous solution of potash (strong, according to Völckel) or carbonate of potash, yields sulphide, cyanide, and sulphocyanide of potassium. (Liebig & Wöhler) :

$$2C^2NH^2S^2 + 4KO = 2KS + C^2NK + C^2NKS^2 + 4HO.$$

But when boiled with dilute potash, it yields ammonia, sulphide of potassium, and oxalate of potash:

$$C^4N^2H^4S^4 + 6KO + 2HO = 2NH^3 + 4KS + C^4K^2O^8.$$

5. Dilute hydrochloric acid acts in a similar manner, forming sal-ammoniac, hydrosulphuric acid, and oxalic acid (Völckel):

$$C^4N^2H^4S^4 + 8HO + 2HCl = 2NH^4Cl + 4HS + C^4H^2O^8.$$

6. With nitrate of silver, bihydrosulphate of cyanogen forms a black precipitate of sulphide of silver, with evolution of cyanogen and nitric acid (Wöhler):

$$C^2NH^2S^2 + 2(AgO,NO^5) = 2AgS + 2HO + C^2N + 2NO^5.$$

7. Heated with peroxides, this compound yields hydrocyanic acid and a soluble sulphocyanide. (Liebig & Wöhler.) [?] — 8. Dissolved in aqueous hydrosulphate of potassium, it yields sulphocyanide of ammonium, and a brown substance like paracyanogen. (Völckel.)—The compound is not decomposed by dry hydrochloric acid gas, even at 100°; or by sulphurous acid; or by ammonia, either in the gaseous state or dissolved in water; and not even when its aqueous solution is boiled with mercuric oxide.

(Völckel.) It likewise dissolves, without decomposition, in cold potash-ley. (Wöhler.)

Combinations. Bihydrosulphate of cyanogen dissolves but very sparingly in cold *Water*, somewhat more abundantly in boiling water, from which it crystallizes on cooling. (Wöhler.)

It dissolves in *Oil of Vitriol*, forming a yellow solution, from which water precipitates it in its original state. (Wöhler.)

It dissolves in *Alcohol* (Wöhler), and in *Ether*, somewhat more readily than in water. (Völckel.)

Compounds with Metals. In these compounds, according to Völckel, 1 At. H. is replaced by 1 At. metal.

Potassium-compound.—Bihydrosulphate of cyanogen dissolves very abundantly in cold dilute potash, forming a yellow liquid, from it is reprecipitated by acids in its original state. The solution does not contain either sulphide or sulphocyanide of potassium. When evaporated at ordinary temperatnres, it yields a large number of small crystals, but becomes continually deeper in colour (when heated it immediately assumes a dark colour), and is afterwards found to contain sulphide, cyanide, and sulphocyanide of potassium. (Wöhler.) This solution is supposed by Völckel to contain the compound C^2NHS,KS.

The aqueous solution of the bihydrosulphate of cyanogen does not precipitate zinc or iron-salts. (Wöhler.)

Lead-compound.—The aqueous solution of bihydrosulphate of cyanogen forms, with acetate of lead, a thick orange-yellow precipitate, which retains its colour when carefully dried, but if somewhat strongly heated, even by boiling with water, is converted into black sulphide of lead. Aqueous potash instantly converts it into sulphide of lead, while cyanide and sulphocyanide of potassium pass into the solution. Boiling hydrochloric acid forms, with the lead compound, a yellowish red solution, from which alcohol throws down the chloride of lead which has been formed, the undecomposed hydrosulphate of cyanogen remaining in solution. (Wöhler.)—Völckel precipitates the acetate of lead solution with an excess of alcoholic hydrosulphate of cyanogen; for an excess of the lead-salt partially decomposes the precipitate, especially if the liquid be not quickly filtered off. The precipitate may be dried by heat. In the decomposition which takes place on boiling with water, there are produced, according to Völckel, sulphide of lead, cyanogen gas, and a solution containing both yellow and red hydrosulphate of cyanogen, according to the equation:

$$5C^2NHPbS^2 = 5PbS + 2C^2N + C^4N^2H^3S^3 + C^2NH^2S^2.$$

(Völckel).—[It is remarkable, that when the cyanogen is in excess, part only of the red hydrosulphate of cyanogen is converted into the yellow compound, perhaps according to the equation:

$$3C^2NHPbS^2 = 3PbS + C^2N + C^4N^2H^3S^3].$$

		Völckel.		Wöhler.
2 C	12	7·36	7·40	
N	14	8·59	8·56	
H	1	0·62	0·73	
Pb	104	63·80	64·24	64·25
2 S	32	19·63		
	163	100·00		

Copper-compound.—The aqueous solution of the bihydrosulphate forms, with cupric salts, a blackish green precipitate, which behaves like the lead precipitate. (Wöhler.)

Mercury-compound.—The aqueous solution, mixed with cyanide of mercury, yields, with evolution of hydrocyanic acid, a white precipitate which soon turns grey; with corrosive sublimate, it eliminates hydrochloric acid, and forms a thick white precipitate. (Wöhler.)

Copulated Compound.

Sulphocyanide of Methyl. $C^2H^3S,C^2NS=C^2H^3,C^2NS^2$.

CAHOURS. 1846. *N. Ann. Chim. Phys.* 18, 261; also *Ann. Pharm.* 61, 96; abstr. *Compt. rend.* 22, 364.

Schwefelcyanmethyl, Schwefelcyan-Schwefelformafer, Sulfocyanure de methyle.

Obtained by distilling equal parts of sulphocyanide of potassium and sulphomethylate of lime in the state of concentrated aqueous solution, and rectifying the yellowish liquid which settles at the bottom of the watery distillate, after drying it over chloride of calcium:

$$C^2NKS^2 + C^2H^3CaO^2,2SO^3 = C^4NH^3S^2 + KO,SO^3 + CaO,SO^3.$$

As the mixture jumps very violently, a retort of ten times its capacity must be used, and the ebullition kept very moderate to prevent spirting over; the first 90 per cent. goes over at 132°–133°, but ultimately the boiling point rises to 137°–138°.

Transparent and colourless liquid, of sp. gr. 1·115 at 16°. Boils between 132° and 133°. Vapour-density from 2·549 to 2·570. Smells like garlic, and produces some degree of giddiness.

						Vol.	Density.
4 C	24	32·88	33·12	C-vapour	4	1·6640
N	14	19·18	19·14	N-gas	1	0·9706
3 H	3	4·11	4·19	H-gas	3	0·2079
2 S	32	43·83	43·97	S-vapour	½	2·2186
C^2H^3S,C^2NS	73	100·00	102·42		2	5·0611
					1	2·5306

It is Wood-spirit + Hydrosulphocyanic acid — 2 Water. $C^2H^4O^2 + C^2NHS^2 = C^4NH^3S^2 + 2$ Aq.

Chlorine acts upon it gradually, forming, even in daylight, fine crystals of fixed chloride of cyanogen, and a large quantity of a heavy yellow oil, which solidifies in contact with ammonia.—Cold aqueous potash exerts scarcely any action on it, but alcoholic potash, when heated with it, eliminates ammonia and $C^2H^3S^2$ (p. 283), leaving a residue of cyanide of potassium and carbonate of potash [?]. An alcoholic solution of sulphide of potassium decomposes this compound ether, yielding $C^2H^3S^2$ and sulphocyanide of potassium:

$$C^4NH^3S^2 + KS^2 = C^2H^3S^2 + C^2NKS^2.$$

Aqueous ammonia converts it with tolerable rapidity into a brown mould-like substance, and a small quantity of a crystalline body.

Sulphocyanide of methyl is slightly soluble in water, to which it imparts its peculiar odour. It dissolves in warm and tolerably strong nitric acid, and crystallizes out again completely on cooling. Mixes in all proportions with alcohol and ether. (Cahours.)

Selenocyanides. C^2NMSe^2.

BERZELIUS (1820). *Schw.* 31, 60.
CROOKES (1851). *Chem. Soc. Qu. J.* 4, 12.

¶ *Hydroselenocyanic acid.* C^2NHSe^2.—When finely divided selenocyanide of lead is suspended in a warm aqueous solution of the same salt, and subjected to a rapid stream of sulphuretted hydrogen, sulphide of lead is formed, and hydroselenocyanic acid obtained in solution; the filtered liquid must be heated nearly to its boiling point to expel the excess of sulphuretted hydrogen, and again filtered from a small quantity of precipitated selenium.—The solution of hydroselenocyanic acid, thus obtained, is a highly acid liquid, easily decomposed by boiling or by exposure to the air. It cannot be concentrated without decomposition, even over sulphuric acid in vacuo. The addition of almost any acid causes an immediate precipitate of selenium, hydrocyanic acid remaining in solution. It dissolves iron and zinc with evolution of hydrogen, and displaces carbonic acid from the carbonates. (Crookes.)

Calculation.

2 C	12	17·91
N	14	20·90
H	1	1·49
2 Se	40	59·70
C^2NH,Se^2	67	100·00

All the salts of this acid may be formed from it by direct combination.

Selenocyanide of Ammonium.—Obtained by neutralizing the free acid with ammonia.—Crystallizes in minute needles very similar to those of the potassium-salt. Very deliquescent. (Crookes.) ¶

Selenocyanide of Potassium. C^2NK,Se^2.—1. When ferrocyanide of potassium is fused with selenium in a retort, nitrogen is evolved, and perhaps, also, selenide of carbon. The residue is a mixture of selenide of iron and selenide of potassium, from which the latter may be dissolved out by water; and on evaporating the water, anhydrous crystals are obtained, which in form and taste exactly resemble the sulphocyanide. (Berzelius.) — ¶ Crookes fuses 1 pt. of selenium with 3 pts. of dry ferrocyanide of potassium, in a small retort; digests the resulting greenish black mass with absolute alcohol; passes carbonic acid through the solution to decompose cyanide of potassium and cyanate of potash, and precipitates the potash in the form of bicarbonate (a salt which is quite insoluble in absolute alcohol); then distils off the alcohol, together with the hydrocyanic and cyanic acids; and leaves the watery extract of the residue to crystallize in vacuo over oil of vitriol.—The formation of the salt is expressed by the following equation:

$$C^6N^3K^2Fe + 4Se = 2C^2NKSe^2 + FeC^2 + N.$$

The residue in the retort consists principally of carbide of iron, together with undecomposed ferrocyanide of potassium and traces of selenium. As Crookes used an excess of ferrocyanide of potassium, he did not observe the evolution of selenide of carbon mentioned by Berzelius, ¶.—2. This salt may also be obtained by dissolving selenium in cyanide of potassium. (Wiggers.)

Selenocyanide of potassium forms needle-shaped crystals, like those of the sulphocyanide. (Berzelius; Crookes.) They fuse when heated, and are not decomposed by ignition out of contact with the air. (Berzelius.) Heated in a close vessel, they fuse without decomposing, and form a clear liquid which solidifies in a crystalline mass on cooling; but if the air has access to the salt, it decomposes at a temperature a little below 100°. (Crookes.) It is deliquescent (Berzelius, Crookes), and dissolves in water even more readily than the sulphocyanide. (Crookes.) It has a strong alkaline reaction, and its solution in water is accompanied by great depression of temperature. (Crookes.)

			Crookes.
K	39·2	27·00	27·00
Cy	26·0	17·91	
2 Se	80·0	55·09	54·75
$KCySe^2$	145·2	100·00	

The aqueous solution is decomposed by nearly all acids, hydrocyanic acid being evolved and selenium precipitated. (Crookes.)—From the yellowish solution, acids and salts with weak bases, such as ferric sulphate (in which case, however, the base is precipitated, together with the red body), throw down a red substance resembling selenium, an offensive odour being at the same time evolved. When such a mixture is distilled, there passes over a watery liquid which has an insupportable odour, tastes fiery and aromatic at first, and disagreeably bitter afterwards. This liquid does not redden litmus, and cannot, therefore, be hydroselenocyanic acid; the residue of the distillation contains an ammoniacal salt. (Berzelius.)

The aqueous solution of selenocyanide of potassium is decomposed, not only by the stronger mineral acids, but likewise by oxalic, tartaric, and acetic acid, the last, however, acting but slowly at ordinary temperatures; the liquid assumes first a yellow, then an orange colour, and deposits a scarlet powder of selenium, while hydrocyanic acid is set free. Chlorine, added to the aqueous solution, likewise throws down selenium, and forms chloride of cyanogen. (Lassaigne, *J. Chim. méd.* 16, 618.)

¶ *Selenocyanide of Sodium.*—Obtained by neutralizing hydroselenocyanic acid with carbonate of soda. — Alkaline and very soluble; when evaporated in vacuo, it crystallizes in small foliated crystals. (Crookes.)

Selenocyanide of Barium.—Obtained by dissolving carbonate of baryta in the acid, and evaporating over oil of vitriol in vacuo. Not obtained in any definite crystalline form. (Crookes.)

Selenocyanide of Strontium.—Obtained like the barium-salt; crystallizes in well defined prisms. (Crookes.)

Selenocyanide of Calcium.—Crystallizes in groups of stellate needles.

Selenocyanide of Magnesium.—Dries up to a gummy mass, apparently destitute of crystalline structure.

Selenocyanide of Zinc.—This salt may be obtained by dissolving either the metal or its oxide in hydroselenocyanic acid; it forms groups of prismatic needles, which are not deliquescent.

Selenocyanide of Lead. C^2NPb,Se^2. — Selenocyanide of potassium forms, with acetate of lead, a lemon-yellow precipitate, which dissolves, with slight decomposition, in boiling water. The filtered solution, which is neutral to test paper, deposits, on cooling, beautiful lemon-coloured needles which are insoluble in alcohol. The salt may be heated to 100° without decomposition, but assumes, when moist, a slight pink tint. The crystals are extremely light. (Crookes.)

			Crookes.
2 C	12	5·71	5·72
N	14	6·67	
Pb	104	49·52	49·22
2 Se	80	38·10	
C^2NPb,Se^2	210	100·00	

Selenocyanide of Iron.—The rapid decomposition which hydroselenocyanic acid undergoes in contact with stronger acids, prevents the formation of any red colour with ferric salts by double decomposition. Neither, according to Crookes, is a selenocyanide of iron obtained by treating the sesquioxide with hydroselenocyanic acid, selenium being immediately precipitated. On one occasion, however, in preparing selenocyanide of potassium by the process already given (p. 122), the fused mass having been treated with absolute alcohol in a well closed flask, and filtering, a deep blood-red liquid was obtained, the colour of which soon disappeared on exposure to the air, with deposition of selenium. On other occasions, no colour was obtained, the iron always remaining as a black powder, chiefly consisting of carbide of iron. (Crookes.)

Selenocyanide of Copper. — Selenocyanide of potassium added to sulphate of copper throws down a brownish precipitate, which is probably the selenocyanide of copper. It is rapidly decomposed, even at ordinary temperatures, yielding black selenide of copper, with separation of hydroselenic acid. (Crookes.)

Selenocyanide of Mercury with Protochloride of Mercury. $HgCySe^2,HgCl$. —Obtained by adding an excess of protochloride of mercury to selenocyanide of potassium. When strong solutions are used, the whole immediately solidifies into a felt-like mass of yellowish crystals; these, after washing with water, are purified by recrystallization from alcohol. The crystals are but sparingly soluble in cold water, but dissolve more readily in hot water, still more in alcohol and in dilute hydrochloric acid; the latter, however, separates selenium after a while. Nitric acid and aqua-regia dissolve the double salt entirely, the liberated selenium being immediately oxidized. The crystals are anhydrous, and may be heated to 100 without decomposition; above that temperature, they are decomposed, intumescing in a remarkable manner. (Crookes.)

			Crookes.
2 Hg	200·0	58·58	58·47
Cy	26·0	7·62	
2 Se	80·0	23·43	23·93
Cl	35·4	10·37	10·38
$HgCySe^2,HgCl$	341·4	100·00	

All attempts to produce the simple selenocyanide of mercury failed, the double salt just described being always produced. (Crookes.)

Selenocyanide of Silver. C^2NAg,S^2. — Selenocyanide of potassium forms with nitrate of silver a precipitate resembling chloride of silver in appearance. If however the silver-solution be previously mixed with ammonia, the selenocyanide of silver is precipitated in beautiful minute crystals, having the appearance of satin. This salt blackens readily on exposure to light; is insoluble in water, and very sparingly soluble in cold dilute acids. It is instantly decomposed by boiling with strong acids; and unless oxidizing acids are used, selenium is precipitated. (Crookes.)

				Crookes.
2 C	12		5·61	
N	14		6·54	
Ag	108		50·47	50·24
2 Se	80		37·38	37·09
C^2NAg,Se^2	214		100·00	¶.

Tellurocyanide of Potassium?

Tellurium fused with cyanide of potassium yields a uniform mass, from which water extracts pure cyanide of potassium, separating the tellurium in the state of powder. (Berzelius, *Lehrb.*) By fusing tellurium with ferrocyanide of potassium, a black mass is obtained, from which, when digested in water, the tellurium likewise separates in the form of a black powder. (Berzelius, *Schw.* 31, 62.)

¶ Nitroprussides.

PLAYFAIR. *Phil Trans.* 1849, II, 477; *Phil. Mag. J.* 36, 197, 271, and 348; abstr. *Laur. & Gerh. C. R.* 1850, 170; *J. pr. Chem.* 50, 36; *Jahresber.* 1849, 292.

GERHARDT. On the composition of certain Cyanides. *Laur. & Gerh. C. R.* 1850, 145.

The formation of these compounds has been already noticed. (VII, 461, 462.) It had been observed by Gmelin and others that, on mixing a solution of ferrocyanide of potassium with dilute nitric acid, the liquid assumes a coffee-colour; and on adding to this mixture an aqueous solution of sulphide of potassium, sulphur is precipitated, and the liquid assumes a magnificent blue or purple colour. More recently (1849) Playfair has shown that this colouring is due to the decomposition of a new compound, a *Nitroprusside*, formed by the action of the nitric acid on the ferrocyanide of potassium.

The action of nitric acid on the ferrocyanide in the state of powder is similar, but much more violent. Nitric oxide is at first evolved; but, if the mixture be cooled, the disengagement of this gas soon ceases, and is followed by an abundant evolution of cyanogen, hydrocyanic acid, nitrogen, carbonic acid, and a peculiarly irritating gas, probably cyanic acid. The dark red solution deposits, on cooling, abundance of nitre, and afterwards, if the excess of acid be not too great, about 5 per cent. of

oxamide. The solution now forms a deep blue precipitate with ferrous salts; but after being warmed, or even left to stand for several days without warming, it forms with the same salts a dark green or slate-coloured precipitate, and with cupric salts a copious green precipitate. These precipitates are nitroprussides.

During the reaction just described, nitric oxide disappears, not being evolved in the gaseous state, excepting when the action is too violent; the nitric oxide appears therefore to play an important part in the reaction. Now this gas is readily absorbed by cyanide of potassium, the liquid turning red, and depositing a substance like paracyanogen. The solution thus formed does not of itself produce any blue colour with the alkaline sulphides, but on the addition of a ferrous salt, which converts the cyanide into ferrocyanide, the colour is immediately produced. The same effect takes place on adding cyanide of potassium to a solution of green vitriol, saturated with nitric oxide. Hence it appears that the nitroprussiates are formed by *the action of nitric oxide on the ferrocyanides.* A neutral solution of ferrocyanide of potassium is not however perceptibly affected by passing nitric oxide into it; but if the ferrocyanide has been previously mixed with a sufficient quantity of acid to take hold of the base, the nitric oxide is absorbed, provided the solution be warm, and the liquid then gives the deep blue colour with alkaline hydrosulphates. The other ferrocyanides mixed with acids yield similar results; so likewise does ferroprussic acid, when nitric oxide is passed into its aqueous solution, heated over the water-bath. Under these circumstances, the ferroprussic acid is first converted into ferriprussic acid, a change which is made evident by the deep blue colour which the liquid gives with ferrous salts; but as the action of the nitric oxide goes on, the liquid gives, with ferrous salts, precipitates of a paler and paler colour, and ultimately of a clear salmon colour. In this state, the solution consists of nitroprussic acid, and will yield the nitroprussides of the different metals by neutralization.

Considerable uncertainty exists respecting the constitution of the nitroprussides, and consequently as to the precise nature of the reaction on which their formation depends. Playfair deduces from his numerous analyses the general formula $Fe^5Cy^{12}(NO)^3,5M$, and expresses the formation of nitroprussic acid by the action of nitric acid on ferrocyanide of potassium by the equation:

$$8K^2FeCy^3 + 19(HO,NO^5) = Fe^5Cy^{12}(NO)^3,5H + 16(KO,NO^5) + FeCy + Fe^2O^3 + 2HCy + 9Cy + 12HO.$$

According to this equation, 10·04 pts. of iron in the ferrocyanide should be converted into nitroprussic acid; the mean of Playfair's experiments gives 10·2 pts. for the quantity actually converted. Playfair is, however, of opinion that the above formula, though it agrees best with the results of his analyses, is too complex to be the true expression of the constitution of the nitroprussides; and he regards as not improbable the simpler formula $Fe^2Cy^5NO,2M$, which requires $\frac{1}{24}$ more carbon. This latter formula also agrees best with Kyd's analysis of nitroprusside of sodium (*q.v.*) According to both these formulæ, a portion of the cyanogen, viz., $\frac{1}{2}$ according to the former, and $\frac{1}{6}$ according to the latter, is replaced by nit*rous* oxide, a substitution which must be regarded as somewhat improbable. Gerhardt, on the other hand, supposes that the nitroprussides contain nit*ric* oxide, NO^2, and assigns to them the formula $Fe^2Cy^5,NO^2,2M$. It will be seen from the details hereafter to be given *that this formula* agrees upon the whole with the results of analysis, quite

as well as Playfair's, especially in the determinations of the iron and the basic metal. In some of the salts, it gives rather more carbon than the analysis justifies; but the differences are never very great, and are found chiefly in those salts whose purification presents the greatest difficulties. Some of the nitroprussides, in fact, are very unstable, and exhibit a strong tendency to take up small quantities of other cyanides, and crystallize with them without alteration of form; such salts must evidently be very difficult to purify, and therefore it is scarcely to be expected that their constitution, as deduced from analysis, should agree very closely with the general formula of the class to which they belong.

That the nitroprussides really contain NO^2 rather than NO is confirmed by the following facts: (1), That nitroprusside of sodium, when exposed to sunshine, actually gives off NO^2 (Overbeck); and (2), That when a solution of nitroprusside of barium is treated with red oxide of mercury, part of the nitrogen is converted into nitric acid. (*Jahresber.* 1849, 295.)

According to Gerhardt's formula, the formation of nitroprussic acid from ferrocyanide of potassium must be supposed to take place as follows. The ferrocyanide of potassium (or ferroprussic acid) is first converted into ferriprussic acid by the action of nitric oxide (vid. p. 126):

$$4H^2FeCy^3 + NO^2 = 2H^3Fe^2Cy^6 + 2HO + N;$$

and the ferriprussic acid, by the further action of the nitric oxide, is converted into nitroprussic acid:

$$H^3Fe^2Cy^6 + NO^2 = Fe^2Cy^5,NO^2,2H + HCy.$$

The cyanogen, carbonic acid, &c., disengaged in the action, must be regarded as secondary products derived from the action of the nitric acid on the hydrocyanic acid.

Barreswil (*N. J. Pharm.* 17, 441) attributes the formation of nitroprussic acid from ferrocyanide of potassium to the action of hyponitric acid, formed from the nitric oxide by oxygen, derived from the air. According to his experiments, ferrocyanide of potassium [neutral ?] is not decomposed by nitric oxide.

Preparation. The nitroprussides of potassium and sodium are obtained as follows: 422 gr. (2 At.) pulverized ferrocyanide of potassium is mixed with 5 At. commercial nitric acid diluted with its own bulk of water (the strength being determined by an alkalimetric process). One-fifth of this quantity (1 At.) of acid is actually sufficient to transform the ferrocyanide into nitroprusside, but the use of the larger quantity is found to give the best results. The acid is poured all at once upon the ferrocyanide, the cold produced by the mixing being sufficient to moderate the action. The mixture first assumes a milky appearance; but after a little while the salt dissolves, forming a coffee-coloured solution, and the gases above-mentioned are disengaged in abundance. When the salt is completely dissolved, the solution is found to contain ferridcyanide (red prussiate) of potassium, mixed with nitroprusside and nitrate of the same base. It is then immediately decanted into a large flask, and heated over the water-bath; it continues to evolve gas, and, after a while, no longer yields a dark blue precipitate with ferrous salts, but a dark green or slate-coloured precipitate. It is then removed from the fire, and left to crystallize; whereupon it yields a large quantity of crystals of nitre, and more or less oxamide. The strongly coloured mother-liquid is then neutralized with

carbonate of potash or soda, according to the salt to be prepared, and the solution is boiled, whereupon it generally deposits a green or brown precipitate, which must be separated by filtration. The liquid then contains nothing but nitroprusside and nitrate of potash or soda. The nitrates being the least soluble are first crystallized out; and the remaining liquid, on further evaporation, yields crystals of the nitroprusside. The sodium-salt crystallizes most easily.

The insoluble nitroprussides, those of iron, copper, silver, zinc, &c., are obtained by precipitating the solutions of the potassium or sodium-salt, with solutions of the respective metals; and the ammonium, barium, calcium, and magnesium salts, which are soluble, by decomposing the iron or copper salt with a solution of caustic ammonia, baryta, or lime. (Playfair.)

Properties and Decompositions. The nitroprussides are in general strongly coloured. The ammonium, potassium, sodium, barium, calcium, and lead-salts, are of a deep red or ruby colour; they dissolve readily in water, imparting to it a strong red tint. Alcohol does not precipitate these salts from their solution. The soluble nitroprussides crystallize easily, and yield well defined crystals. The nitroprussides of zinc, iron, cobalt, nickel, copper, and silver, are either very sparingly soluble, or completely insoluble.

Some of the nitroprussides are very permanent, and suffer no change in solution, either by exposure to the air or by the action of heat. Several, on the contrary, especially nitroprussic acid, and the nitroprussides of ammonium, barium, and calcium, undergo partial decomposition when their solutions are long kept, and rapid alteration when boiled; they then deposit prussian blue or oxide of iron. The remaining liquid yields, by evaporation, crystals having exactly the same form and properties as the original salt. Their composition is however somewhat altered, the iron being in greater proportion than before; and the proportion of carbon also slightly different. These differences appear to be due to an impurity, probably a cyanide of iron, which cannot be removed by crystallization, precipitation, or any other means. Several of the nitroprussides, viz., nitroprussic acid, and the ammonium and calcium-salts, have not yet been obtained free from this impurity.

Sulphuretted hydrogen decomposes the soluble nitroprussides, a precipitate being gradually formed, containing sulphur, prussian blue, and a ferrocyanide, and the supernatant brown liquid containing a peculiar sulphur-compound, whose nature has not yet been determined. The *Sulphides of the Alkali-metals* added, even in very small quantity, to a solution of a nitroprusside, immediately produce a magnificent blue or purple colour, affording a highly characteristic test for this class of salts; it is so intense, that it serves to discover the least trace of a nitroprusside, or, on the other hand, of a soluble sulphide. It is however but transient, at least in aqueous solutions, the new product being quickly resolved into a number of other bodies, among which may be recognized hydrocyanic acid, ammonia, nitrogen, an oxide of iron, a ferrocyanide, a sulphocyanide, and a nitrate. On mixing the alcoholic solutions of nitroprusside and protosulphide of sodium, the purple compound is precipitated in oily drops, which generally dry up in vacuo to a green powder, consisting of the purple compound mixed with the products of decomposition just mentioned (vid. *Nitroprusside of Sodium*). — *Sulphurous acid*, the *Sulphites*, and *Hyposulphites*, do not exert any perceptible action on the nitro-

prussides; but *strong sulphuric acid* decomposes them, producing the same blue colour as the sulphides.—*Chlorine* exerts no action on the nitroprussides.

Ammonia in excess gradually decomposes the nitroprussides, even at ordinary temperatures, nitrogen being given off, and a black uncrystallizable substance remaining.—*Caustic alkalis* change the red colour of the soluble nitroprussides to orange; on boiling the mixture, the salt is decomposed, yielding sesquioxide of iron, a ferrocyanide, a nitrate, and nitrogen gas; *e.g.* with nitroprusside of sodium:

$$2(Fe^5Cy^{12},3NO,5Na) + 9NaO = 8Na^2FeCy^3 + 3(NaO,NO^3) + Fe^2O^3 + 3N.$$

Zinc-salts form with the solutions of the nitroprussides, a precipitate of a clear salmon-colour;—*Stannous* and *Stannic* salts produce no change;—*Neutral Lead-salts*, no change;—*Basic Lead-salts*, a white precipitate after a while, but only in concentrated solutions;—*Ferrous* salts, a salmon-coloured precipitate;—*Ferric* salts, no change;—*Cobalt*-salts, a flesh-coloured precipitate; — *Nickel*-salts, dirty-white; and *Copper*-salts, light green;—Mercuric salts produce no change;—Silver-salts, a reddish white precipitate. (Playfair.)

Combinations. Most nitroprussides contain *Water of crystallization*, and many of them dissolve very readily in water.—*Prussian blue* dissolves in the solutions of many of these salts, imparting a fine blue colour to the liquid. The nitroprussides exhibit also a strong tendency to unite with other cyanides. Some of them also combine with the oxides and sulphides of the alkali-metals. (Playfair.)

Nitroprussic Acid.—1. Obtained by decomposing the silver-salt with an equivalent quantity of hydrochloric acid, or the baryta-salt by an equivalent quantity of sulphuric acid.—2. By adding to nitroprusside of potassium, dissolved in a small quantity of water and mixed with several times its volume of alcohol, a quantity of tartaric acid dissolved in alcohol, just sufficient to precipitate all the potassium in the form of bitartrate. This process does not yield a pure product, because the acid dissolves some of the cream of tartar.—Either of these processes yields a dark red, strongly acid liquid, which, when evaporated in vacuo, yields the acid in dark red, very deliquescent crystals, having the form of oblique prisms. They are very soluble in water, alcohol, and ether. The aqueous solution decomposes spontaneously at ordinary temperatures, yielding ferric oxide, hydrocyanic acid, and a soluble iron-salt which may be detected by a ferrocyanide. In consequence of the proneness of the solution to decomposition, the crystals obtained from it are never quite pure. (Playfair.)

Calculation (*a*).			*Calculation* (*b*).			Playfair.
24 C	144	24·9	10 C	60	25·4	24·8
15 N	210	36·4	6 N	84	35·6	36·7
5 Fe	140	24·3	2 Fe	56	23·7	23·8
11 H	11	1·9	4 H	4	1·7	1·7
9 O	72	12·5	4 O	32	13·6	
$Fe^5Cy^{12}(NO)^3H^5 + 6Aq$	577	100·0	$Fe^2Cy^{15},NO^2,H^2 + 2Aq$	236	100·0	

In this and the following tables, *Calculation* (*a*) is made according to Playfair's formula, and *Calculation* (*b*) according to Gerhardt's (vid. p. 126); the last column gives the *mean* results of Playfair's analysis.

Nitroprusside of Ammonium.—When ammonia is added to an excess of nitroprusside of iron, oxide of iron is separated, nitrogen evolved, and a red solution formed, which, when evaporated in vacuo, yields a difficultly crystallizable salt. The solution when heated, deposits prussian blue, and afterwards yields dark red, rhombic crystals of a somewhat altered salt, which gave by analysis, 22·6 per cent. of carbon; 45·9 nitrogen; 22·1 iron, and 3·2 hydrogen;—The formula $Fe^5Cy^{12}(NO)^3(NH)^4H^5+6Aq$. requires 23·0 C, 44·7 N, 22·3 Fe, and 3·5 H;—and Gerhardt's formula, $Fe^2Cy^5,NO^2,(NH^4)^2$, requires 23·8 C; 44·4 N; 22·2 Fe; and 3·1 H.—Playfair regards the first mentioned salt as the true nitroprusside of ammonium, which, however, from its proneness to decomposition, he could not obtain sufficiently pure for analysis; and the dark red salt whose composition is above given, as a product of its decomposition. (Playfair.)

Nitroprusside of Potassium.—1. Obtained by acting upon ferrocyanide of potassium with dilute nitric acid, and neutralizing the resulting nitroprussic acid with carbonate of potash (vid. p. 127);—2. By decomposing nitroprusside of iron (or better, the copper-salt) with caustic potash.

Very soluble, and therefore difficult to crystallize. The crystals are oblique prisms. The salt dissolves in its own weight of water at 16°. It turns greenish on exposure to light, and its solutions undergo partial decomposition when kept for some time. The crystals when heated over the water-bath give off 11·7 p. c. water. The composition of the salt dried at 100° is as follows (Playfair):

Calculation (a).			*Calculation (b).*			Playfair.
24 C	144	19·4	10 C	60	20·4	19·6
15 N	210	28·4	6 N	84	28·6	
5 Fe	140	18·9	2 Fe	56	19·0	19·05
5 K	195	26·3	2 K	78	26·5	26·4
3 H	3	0·4				0·7
6 O	48	6·6	2 O	16	5·5	
$Fe^5Cy^{12}(NO)^3K^5+3HO$	740	100·0	Fe^2Cy^5,NO^2,K^2	294	100·0	

Nitroprusside of Potassium with Potash.—When an aqueous solution of nitroprusside of potassium is mixed with twice its volume of alcohol, and caustic potash added, a yellow precipitate is formed, which is very slightly soluble in alcohol, but dissolves readily in water. The solution has a strong alkaline reaction, forms a bright yellow precipitate with lead-salts, yellowish brown with iron-salts, and brown with copper-salts. This precipitate, when treated with acids, is resolved into nitroprusside of potassium and a salt of potash. (Playfair.)

Calculation.			Playfair.
24 C	144	14·8	15·0
15 N	210	21·6	
5 Fe	140	14·4	13·7
9 K	351	36·1	36·6
8 H	8	0·8	
15 O	120	12·3	
$Fe^5Cy^{12}(NO)^3,K^5+4KO+8HO$	973	100·0	

Nitroprusside of Sodium. 1. Obtained by decomposing ferrocyanide of potassium with nitric acid, and neutralizing the resulting nitroprussic

acid with carbonate of soda (p. 126). On evaporating the dark red solution which remains after the nitrates of potash and soda have crystallized out, prismatic crystals separate during the evaporation from the hot solution. These are removed, dissolved in water, and again crystallized by allowing the solution to cool. The object of taking the crystals from the hot solution is to obtain them uncontaminated with nitrates, which are more soluble in hot water than the nitroprusside.—2. By treating the nitroprusside of iron or copper with caustic soda. When prepared from the iron-salt, it is apt to contain a little iron in excess.

Crystallizes in large ruby-coloured oblique prisms, very much resembling the ferricyanide of potassium crystallized from an alkaline solution. (For details respecting the crystalline form, vid *Phil. Mag. J.* 36, 210; also Rammelsberg, *Pogg.* 87, 107.) It is the most easily crystallized of all the nitroprussides. It is not deliquescent, but dissolves very readily in water; 1 pt. of the salt dissolves in $2\frac{1}{2}$ pts. of water at 15°, and in a still smaller quantity of hot water. It does not lose weight at 100°. (Playfair.)

Calculation (a).			Playfair.		Kyd.
24 C	144	19·9	19·5	20·4	20·2
15 N	210	29·0	27·8	28·8	27·8
5 Fe	140	19·3	19·3	19·9	19·3
5 Na	116	16·0	15·2	16·3	15·5
10 H	10	1·3	1·3	1·6	1·5
13 O	104	14·5			
$Fe^5Cy^{12}(NO)^3,Na^5+10Aq.$	724	100·0			

Calculation (b).		
10 C	60·0	20·1
6 N	84·0	28·1
2 Fe	56·0	18·8
2 Na	46·4	15·4
4 H	4·0	1·3
6 O	48·0	16·3
$Fe^2Cy^5,NO^2,Na^2+4Aq.$	298·4	100·0

Kyd (*Phil. Mag. J.* 37, 289) gives the preference to the formula $Fe^2Cy^5,NO,Na^2+4Aq.$ which requires 20·7 p. c. carbon, 28·9 nitrogen, 19·5 iron, 16·0 sodium, and 1·4 hydrogen. This is certainly preferable in point of simplicity to Playfair's formula, and agrees quite as well with the analytical results; indeed Playfair himself remarks (*Phil. Mag. J.* 36, 360) that the formula Fe^2Cy^5,NO,M^2 may probably be the correct expression for the composition of the nitroprussides. But, on the other hand, Gerhardt's formula gives numbers which, for this salt at least, approach quite as near to the experimental results as either of the two formulæ proposed by Playfair. Moreover there are many reasons for supposing that these salts contain NO^2 rather than NO (*comp.* p. 127).

A solution of nitroprusside of sodium, exposed to sunshine, immediately begins to give off gas, acquiring at the same time a green colour, and depositing prussian blue. The evolution of gas goes on, though slowly, for several days, ceasing as soon as the direct light of the sun is removed, and recommencing as soon as it is restored. The evolved gas, when mixed with pure oxygen, forms red fumes, which condense to a greenish liquid having the properties of hyponitric acid. Hence the gas appears to be nitric oxide, which therefore is most probably contained in the salt; at all events we know of no instance of its being formed from nitrous oxide. (Overbeck, *Pogg.* 87, 110.)

The decomposition of this salt by alkaline sulphides has been already noticed (p. 128). The purple compound obtained by mixing the alcoholic

solutions of nitroprusside and protosulphide of sodium, was found, after drying in vacuo, to contain 17·27 p. c. carbon; 16·84 iron; 22·60 sodium; 0·74 hydrogen; 5·71 sulphur; leaving 36·84 for the nitrogen and oxygen. These numbers agree pretty nearly with the formula $Fe^5Cy^{12}(NO)^3Na^5 + 3NaS^2 + 6Aq.$, which requires 17·27 carbon, 17·36 iron, 23·07 sodium, 0·74 hydrogen, and 5·95 sulphur. The composition of this substance must however be regarded as only approximately determined; for it decomposes very quickly in drying; and many analyses of it in its partially decomposed state yielded the most discordant results. The numbers above given are the mean results of two analyses made on the only specimens which appeared to be unchanged.—The purple-blue unchanged compound yields with ferrous salts a precipitate of the same colour, with lead-salts yellowish brown, and with copper salts a brown precipitate. When dissolved in water, its purple-blue colour soon changes to red, and it then gives a red precipitate with lead-salts. The red solution also decomposes quickly, depositing ferric oxide and sulphur; the supernatant liquid contains a ferrocyanide, a sulphocyanide, and a nitrate, whilst at the same time nitrogen, hydrocyanic acid, and, at a boiling heat, also ammonia, occur as products of the decomposition. Playfair expresses the decomposition by the equation:

$$2(Fe^5Cy^{12}N^3O^3,Na^5 + 3NaS) + 2HO = 7(FeCy^3,Na^2) + CyS^2Na + NaO,NO^3 + Fe^3O^4 + S^4 \quad 2HCy + 5N$$

The ammonia he regards as a secondary product, due to the conversion of the ferrous into ferric oxide (which latter was alone actually observed), at the expense of the elements of water, the hydrogen of the latter combining with the nitrogen to form ammonia.—Proceeding from Gregory's observation that sulphide of nitrogen produces with caustic alkalis a transient amethyst colour, on the disappearance of which ammonia is given off, Playfair thinks it possible that the true formula of the blue compound may be: $Fe^5Cy^{12}N^3S^3,5Na + 3NaO + 6Aq.$ (Playfair.)

Nitroprusside of Barium.—Obtained by decomposing the copper-salt with caustic baryta, avoiding an excess of the latter. The dark red filtrate, evaporated under the air-pump, yields large dark red pyramidal crystals. From concentrated solutions, it sometimes crystallizes in flattened prisms, which appear to be a different hydrate. The pyramidal crystals lose from 14·9 to 15·2 per cent. of water at 100°. The salt dissolves very readily in water. (Playfair.)

Dried at 100°.	*Calculation* (*a*).	
24 C	144	14·5
15 N	210	21·1
5 Fe	140	14·0
5 Ba	343	34·4
15 H	15	1·5
18 O	144	14·5
$Fe^5Cy^{12}(NO)^3,Ba^5 + 15HO$	996	100·0

Dried at 100°.	*Calculation* (*b*).		Playfair.
10 C	60·0	15·4	15·0
6 N	84·0	21·7	
2 Fe	56·0	14·4	14·05
2 Ba	137·2	35·0	34·6
4 H	4·0	1·1	1·35
6 O	48·0	12·4	
$Fe^2Cy^5,NO^2,Ba^2 + 4HO$	389·2	100·0	

Playfair observes that the analysis of this salt agrees better with the formula Fe^2Cy^5,NO,Ba^2+6Aq, which requires 15·0 p. c. carbon, 14·0 iron, 34·3 barium, and 1·5 hydrogen, than with his more complicated formula. But with this, as with the other nitroprussides, it must be remarked that it more probably contains NO^2 than NO; for when its solution is treated with mercuric oxide, part of the nitrogen is converted into nitric acid, a fact scarcely consistent with the existence of the nitrogen as nitrous oxide. (*Jahresber*, 1849, 297.)

When a solution of nitroprusside of barium is heated to the boiling point, a brown powder separates out, containing iron and baryta, and the filtrate yields, on evaporation, crystals having the same form as the unaltered salt, but of variable composition.

Nitroprusside of Calcium. Prepared by decomposing nitroprusside of iron or copper with milk of lime not in excess. A dark red solution is formed, which, on evaporation, even at a gentle heat, deposits prussian blue. When sufficiently concentrated, it yields oblique prismatic crystals of a dark red colour and considerable lustre. The salt is very soluble in water. The crystals, when heated to 100°, lose 17·44 p. c. water, corresponding to 15 At. (Playfair.)

Dried at 100°.			Playfair.
24 C	144	21·7	21·5
15 N	210	31·6	
5 Fe	140	21·1	21·1
5 Ca	100	15·1	14·1
5 H	5	0·7	1·1
8 O	64	9·8	
$Fe^5Cy^{12}(NO)^3,Ca^5+5HO$	663	100·0	

The great facility with which this salt decomposes, throws great obstacles in the way of determining its composition: it is very apt to dissolve some of the cyanide of iron resulting from its decomposition.

Nitroprusside of Zinc.—Soluble zinc-salts form, with solutions of the nitroprussides, a salmon-coloured precipitate, approaching more nearly to a flesh-colour than the iron-salt. When formed slowly, as when hydrochloric acid and zinc are made to act on nitroprusside of sodium, it has a deep orange colour. Very slightly soluble in cold, more soluble in hot water. (Playfair.)

			Playfair.
24 C	144	20·7	20·5
15 N	210	30·2	
5 Fe	140	20·1	20·1
5 Zn	160	23·0	22·3
2 H	2	0·3	0·4
5 O	40	5·7	
$Fe^5Cy^{12}(NO)^3,Zn^5+2HO$	696	100·0	

Stannous and Stannic salts give no precipitates with soluble nitroprussides.

Neutral Lead-salts give no precipitate; *Basic Lead-salts*, a white precipitate.

Nitroprusside of Iron.—Ferrous salts form a salmon-coloured precipitate with the soluble nitroprussides. If the solutions are dilute, the precipitate does not appear at first. This salt is nearly insoluble in water; more soluble in water acidulated with nitric acid. It is decomposed by caustic alkalis, with separation of oxide of iron and formation

of a soluble nitroprusside; a dark-coloured basic iron-salt is however formed, previously to complete decomposition. The salt, after drying at 32°, lost about 20 per cent. more of water when heated to 100°. (Playfair.)

Dried at 100°.			Playfair.
24 C	144	19·7	20·0
15 N	210	28·8	29·3
10 Fe	280	38·3	38·2
8 H	8	1·1	1·2
11 O	88	12·1	
$Fe^5Cy^{12}(NO)^3,Fe^5+8HO$	730	100·0	

Cobalt-salts yield a flesh-coloured, and *Nickel-salts* a dirty white precipitate with soluble nitroprussides.

Nitroprusside of Copper.—Cupric salts form with soluble nitroprussides, a pale green precipitate which becomes slate-coloured on exposure to light. It is insoluble in water and alcohol, and is decomposed by caustic alkalis, with formation of a soluble nitroprusside. After drying at about 38°, it still lost about 10½ p. c. in the water-bath. (Playfair.)

Dried at 100°.			Playfair.
24 C	144	21·0	21·2
15 N	210	30·7	30·7
5 Fe	140	20·4	20·5
5 Cu	158	23·1	22·8
H	1	0·1	0·3
4 O	32	4·7	
$Fe^5Cy^{12}(NO)^3Cu^5+HO$	685	100·0	

Mercuric-salts give no precipitate with the nitroprussides.

Nitroprusside of Silver.—Soluble nitroprussides form with nitrate of silver, a reddish white precipitate which is readily decomposed by hydrochloric acid and by caustic alkalis.

Calculation (*a*).		
24 C	144	13·4
15 N	210	19·5
5 Fe	140	13·0
5 Ag	540	50·2
2 H	2	0·2
5 O	40	3·7
$Fe^2C^{15}(NO)^3Ag^5+2HO$	1076	100·0

Calculation (*b*),			Playfair.
10 C	60	13·8	13·3
6 N	84	19·4	19·3
2 Fe	56	12·9	13·0
2 Ag	208	50·0	50·1
2 O	16	3·9	
Fe^2Cy^{15},NO^2,Ag^2	424	100·0	

The [illegible] solution of this salt in ammonia deposits, after a while, shining crystals o[illegible] a compound of the salt with ammonia; this compound is quickly decom[illegible]posed, even by water alone, but still more readily by water acidulate[illegible]d with nitric acid. When ammonia and nitroprusside of silver are boiled together, total decomposition takes place. (Playfair.) ¶

Secondary Nucleus C^2NI.

Iodide of Cyanogen. C^2NI.

H. DAVY. *Gilb.* 54, 384.
WÖHLER. *Gilb.* 69, 281.
SERULLAS. *Ann. Chim. Phys.* 27, 184; also *Schw.* 43, 42; also *Pogg.* 2, 334.—*Ann. Chim. Phys.* 29, 184; 34, 100; 35, 293, and 344.
VAN DYK. *Repert.* 21, 223.

Iodcyan, Cyanure d'Iode.—Discovered by H. Davy in 1816.

Formation. By triturating iodine with cyanide of mercury (H. Davy) or cyanide of silver (Wöhler);

$$C^2NHg + 2I = C^2NI + HgI.$$

The reaction is much accelerated by heat. The presence of a small quantity of moisture likewise accelerates the formation of the iodide of cyanogen. (Serullas.) A mixture of 2 pts. cyanide of mercury and 1 pt. iodine heated in a strong sealed glass tube, yields iodide of cyanogen, whose crystals fill up the tube, and liquid cyanogen [proceeding from the decomposition of the excess of mercuric cyanide by the heat] containing in solution a small quantity of iodine which gives it a red colour, but no iodide of cyanogen. (Serullas.) Iodide of cyanogen is not obtained by heating iodine in cyanogen gas; it appears indeed to be formed only by substitution.

Preparation. 1. A mixture of iodine and cyanide of mercury is heated, and the vapour of the iodide of cyanogen condensed in a cooler part of the apparatus.—It is usual to take, according to Serullas's recommendation, 2 pts. of mercuric cyanide to 1 pt. of iodine; but as both these substances have the same atomic weight, viz. 12·6, and moreover 1 At. of the former requires 2 At. of the latter, the proportion by weight should be, on the contrary, 1 pt. of mercuric cyanide to 2 pts. of iodine, or somewhat less, so that the sublimate may not be contaminated by free iodine. (Gm.) — *a.* 2 pts. of cyanide of mercury are mixed with 1 pt. of iodine, very intimately, but quickly, to prevent loss by volatilization, and the mixture gradually and gently heated, either in a retort provided with a receiver, or in a wide-necked flask, the mouth of which passes under a bell-jar partly closed with a glass plate; or the mixture is heated in a small porcelain dish till the iodide of cyanogen begins to volatilize, the dish then placed upon a large glass plate, and covered with a bell-jar; in the course of 15 minutes, the iodide of cyanogen sublimes on the sides of the jar in large white flocks. (Serullas.) — *b.* Van Dyk places over the wide-necked flask in which the mixture is heated, a hollow glass globe, which he replaces by another as soon as it becomes filled with the sublimate. — *c.* Wackenroder (*N. Br. Arch.* 19. 320), in order to prevent the admixture of iodide of mercury, places the mixture in the closed end of a retort-shaped tube; draws out the open end to a fine neck; gradually heats the mixture to 135° in a bath of concentrated chloride of zinc, till the open arm of the tube becomes filled with needles of iodide of cyanogen, which takes place in a few hours; and then closes it at both ends. — *d.* Mitscherlich (*Lehrb.*) adds water to the mixture of mercuric cyanide

and iodine, and heats the liquid to the boiling point.—From the iodide of mercury, which sublimes with the iodide of cyanogen chiefly towards the end of the operation, the product may be freed by a second sublimation over the water-bath or in sunshine, an operation which takes a long time. If the iodide of cyanogen, when supersaturated, first with strong aqueous potash and then with nitric acid, yields no precipitate of mercuric iodide, it may be considered free from that impurity. (Serullas.)

2. By heating a mixture of iodine and cyanide of silver. This process yields a purer product (Wöhler) — 134 pts. (1 At.) cyanide of silver require rather less than 252 pts. (2 At.) of iodine.

3. Iodine is dissolved in a concentrated solution of cyanide of potassium, in such quantity that the solution may solidify in a crystalline mass on cooling, and the solid mass is gently heated till the iodide of cyanogen sublimes. (Liebig, *Chim. org.* 1, 180.)

Properties. Long, white, very delicate needles, loosely united in feathers and stars. (Serullas.) ¶ From its solution in ether or absolute alcohol, this compound crystallizes in small four-sided tables; from a solution in spirit of 80 per cent., in long feathery needles. (Herzog. *Arch. Pharm.* [2], 61, 129; *Jahresber.* 1850, 354.)—¶ Sinks rapidly in oil of vitriol. Boils at a temperature considerably above 100°, and volatilizes undecomposed, even at ordinary temperatures. Has a highly penetrating and pungent odour, of iodine and cyanogen together; excites a copious flow of tears; has an extremely acrid taste (metallic if it is contaminated with iodide of mercury). (Serullas.) Its aqueous solution is neutral towards turmeric and litmus (Serullas, Wöhler), and does not impart any blue colour to starch. (Wöhler). Exerts a very poisonous action, like iodine and cyanogen together.

				Serullas.
2 C	12		7·89	
N	14		9·21	
I	126		82·90	80·66
C^2NI	152		100·00	

Decompositions. 1. Iodide of cyanogen thrown upon red-hot coals (Serullas), or passed through a red-hot tube (Wöhler), gives off violet vapours of iodine. Even its aqueous solution when kept for some time, imparts a pale violet colour to the superincumbent air (Serullas).—*Oil of vitriol* decomposes iodide of cyanogen very slowly, acquiring thereby a red colour, and precipitating iodine (Serullas); according to Herzog, the decomposition does not take place without the aid of heat. — 3. *Sulphurous acid gas* exerts no action on iodide of cyanogen; but the aqueous solution of the acid forms with it (water being decomposed) sulphuric acid, hydrocyanic acid and iodine, which last substance, by the further action of the sulphurous acid yields hydriodic and sulphuric acids. (Serullas):

$$CyI + HO + SO^2 = SO^3 + HCy + I;$$

and:

$$CyI + 2HO + 2SO^2 = 2SO^3 + HCy + HI.$$

Part of the iodide of cyanogen, however, appears to remain undecomposed: for, according to Serullas, the liquid, when freed by boiling from hydrocyanic and hydriodic acids, and heated first with potash, then with green vitriol, and then with hydrochloric acid, yields a green precipitate: — 4. *Hydrochloric acid* decomposes iodide of cyanogen, yielding

hydrocyanic acid and iodine (Serullas). The reaction in this case is by no means evident; according to Wöhler, hydrochloric acid does not exert any decomposing action upon iodide of cyanogen; according to Herzog, the decomposition does not take place without the aid of heat. — 5. *Hydrosulphuric acid gas*, in the absence of water, converts iodide of cyanogen into hydriodic acid and black iodide of sulphur; in presence of water, the products are hydrocyanic acid, hydriodic acid, and a precipitate of sulphur:

$$CyI + HS = HCy + SI;$$

and:

$$CyI + 2HS = HCy + HI + 2S.$$

6. Iodide of cyanogen dissolves in *Caustic potash*, forming cyanide of potassium, iodide of potassium, and perhaps also iodate of potash (Serullas). Probably thus:

$$3CyI + 6KO = 3KCy + 2KI + KO,IO^5.$$

Hence the alcoholic solution imparts a blue colour to starch when mixed with an acid, and yields prussian blue on being mixed with a ferroso-ferric salt, and then with hydrochloric acid. (Wöhler.) Serullas obtained a green precipitate instead of prussian blue.—According to a late observation of Serullas (*Ann. Chim. Phys.* 35, 345), cyanate of potash appears to be formed on adding a small quantity of potash to aqueous iodide of cyanogen; for the mixture, when supersaturated with an acid, gives off carbonic acid, and is afterwards found to contain ammonia. — 7. An aqueous solution of iodide of cyanogen mixed, first with potash, then with *green vitriol*, then with hydrochloric acid, or first with green vitriol, then with potash, and then with hydrochloric acid, yields a green precipitate (Serullas). This reaction distinguishes iodide of cyanogen from the bromide and chloride, which yield the green precipitate in the latter case only. — 8. *Phosphorus* melts in contact with iodide of cyanogen, and yields iodide of phosphorus, often with emission of light and heat; the cyanogen is probably set free in this reaction (Wöhler, Dyk). Similarly, powdered *Antimony* heated with iodide of cyanogen, decomposes it with noise, and forms iodide of antimony; and *Mercury* agitated with aqueous iodide of cyanogen, liberates the cyanogen, and is converted into iodide of mercury, exhibiting first a yellow and then a red colour. (Wöhler.)

Dry chlorine gas and nitric acid do not decompose iodide of cyanogen. (Serullas.)

Combinations. Iodide of Cyanogen absorbs *Water of Crystallization.* (Serullas.)—It dissolves readily in water; the colourless solution has the taste and smell of the compound itself, and does not act on heavy metallic salts, not precipitating a solution of silver for example (Wöhler, Serullas), or of iron, zinc, lead, gold, or platinum. (Herzog.)

¶ Iodine containing iodide of cyanogen forms, with water and metallic iron, a liquid containing ferrous cyanide as well as ferrous iodide; carbonate of potash added to this liquid, throws down all the cyanogen in combination with the iron; so that iodide of potassium thus prepared is free from cyanide, even if the iodine used contains iodide of cyanogen. (Herzog.) ¶

Iodide of cyanogen dissolves without decomposition in aqueous *Sulphuric*, *Nitric*, or *Hydrochloric acid*, forming colourless solutions. (Wöhler, Van Dyk.)

It unites with *Ammonia.* (Bineau.)

It dissolves in *Alcohol* more freely than in water (Serullas), still more readily in *Ether* and in *Volatile Oils*, such as oil of turpentine (Van

Dyk); it likewise dissolves in *Fixed Oils.* (Van Dyk.)—The ethereal solution, when treated with potash, becomes light yellow and turbid, and exhales an odour like that of hydrocyanic acid. (Van Dyk.)

Ammonio-iodide of Cyanogen. $3NH^3,C^2NI$ and NH^3,C^2NI.

1. Iodide of cyanogen slowly absorbs ammoniacal gas, retaining its original appearance for a few days, excepting that a few crystals are deposited upon it; afterwards it changes gradually to a liquid, and in the course of a week becomes completely saturated with ammonia. The reddish yellow colour of the compound probably arises from the separation of a small quantity of iodine in consequence of the air not being completely excluded (Bineau) — ¶. 2. An alcoholic solution of ammonia dissolves iodide of cyanogen in considerable quantity, and afterwards deposits the ammonio-iodide in crystals, which, however, disappear on exposure to the air. (Herzog.) ¶

The liquid when exposed to the air, exhales ammonia abundantly, and solidifies to a crystalline laminated mass; it boils at about 50°, and solidifies with loss of 16 p. c. (2 At.) ammonia. The residue melts at a higher temperature, gives off ammonia, and—in consequence of access of air—free iodine; yields a white sublimate of hydriodate of ammonia; and leaves a yellow residue of mellon, (Bineau, *Ann. Chim. Phys.* 67, 234.)

Liquid.			Bineau.	*Solid compound.*		
$3NH^3$	51	25·12	24·2	NH^3	17	10·06
C^2NI	152	74·88	75·8	C^2NI	152	89·94
$3NH^3,C^2NI$	203	100·00	100·0	NH^3,C^2NI	169	100·00

According to Cloez & Cannizzaro, (*Compt. rend.* 32, 62), the product of the action of iodide of cyanogen on ammonia is a mixture of hydriodate of ammonia and *Cyanamide* Cy, NH^2 (*comp.* p. 145).

Secondary Nucleus C^2NBr.

Bromide of Cyanogen. C^2NBr.

SERULLAS. *Ann. Chim. Phys.* 34, 100; also *Schw.* 49, 246; also *Pogg.* 9, 338.—*Ann. Chim. Phys.* 35, 294 and 335.

K. LOWIG. Das. Brom. u. s. chemischen Verhältnisse. Heidelb. 1829, 69.

Bromcyan, Cyanure de Brome. Discovered by Serullas in 1827.

Preparation. 1. When 1 pt. of bromine is poured upon 2 pts. of cyanide of mercury contained in a tubulated retort or glass tube closed at the bottom and surrounded with ice, bromide of mercury and bromide of cyanogen are formed, with great evolution of heat. The bromide of cyanogen sublimes in needles, contaminated at first with bromine, but ultimately the bromine flows back and enters completely into combination. Gentle heat is then applied, and the bromide of cyanogen sublimed into a receiver connected with the retort and surrounded with ice. (Serullas.) — 2. Aqueous hydrocyanic acid is placed in a vessel surrounded with a frigorific mixture, and bromine added—in very small

portions to prevent the temperature from rising too high—till the solution begins to assume a reddish tinge; the liquid, which is in process of solidification from the acicular crystallization of the bromide of cyanogen, is then either expressed between blotting paper at a temperature below 0°, or it is gently heated to drive off the bromide of cyanogen in vapour, whereupon aqueous hydrobromic acid remains behind. (Löwig.) — 3. Bromine and water are placed in a tube kept very cold, and cyanide of mercury and hydrochloric acid added till the red colour disappears; the open end of the tube is then drawn out to a narrow neck, which is sealed up, and the lower part of the tube is immersed in warm water, so that the bromide of cyanogen may sublime into the upper part. (Mitscherlich, *Lehrb.*)

Properties. Bromide of cyanogen sublimes at the first moment of its formation, in long delicate needles, which afterwards change to small transparent and colourless cubes. (Serullas.) Melts at + 4° (Löwig), above + 16° (Serullas), not even at 40° (Bineau); Vapour-density = 3·607 (Bineau, *Ann. Chim. Phys.* 68, 425). Its boiling point is lower than that of iodide of cyanogen, and it volatilizes even at 15°. (Serullas.) Its vapour has the same pungent odour as the iodide, but in a still higher degree; it excites a copious flow of tears, and is dangerous to inhale (Serullas); its taste is extremely biting (Löwig). One grain dissolved in water and poured into the œsophagus of a rabbit, kills it instantly. (Serullas.) It instantly decolorizes litmus and turmeric paper, and does not redden litmus, even when dissolved in water. (Löwig.)

					Vol.	Density.
2 C	12	11·32		C-vapour	2	0·8320
N	14	13·21		N-gas	1	0·9706
Br	80	75·47		Br-vapour	1	5·5465
C^2NBr	106	100·00			2	7·3491
					1	3·6745

Decompositions. 1. Aqueous *Sulphurous acid* forms with bromide of cyanogen: sulphuric, hydrobromic, and hydrocyanic acids. — 2. Aqueous *Potash* forms cyanide of potassium, bromide of potassium, and bromate of potash. (Serullas, Löwig.) On adding to a saturated solution of bromide of cyanogen, first potash and then an acid, carbonic acid is evolved, and the liquid is afterwards found to contain ammonia. (Serullas.) — 3. The aqueous solution mixed, first with *green vitriol*, then with potash, and then with an acid, yields a green precipitate (Serullas); but if the potash be added first, then the green vitriol, and then the acid, no precipitate is obtained. (Serullas.) — 4. The aqueous solution of bromide of cyanogen, slowly evaporated to dryness, leaves hydrobromate of ammonia. (Löwig.) [In this case carbonic acid should also be produced: $C^2NBr + 4HO = C^2O^4 + NH^4Br$]. — 5. Bromide of cyanogen gently heated with *Phosphorus* evaporates for the most part undecomposed; nevertheless a small quantity of bromide of phosphorus is formed. *Antimony*, heated in vapour of bromide of cyanogen, yields cyanogen gas and bromide of antimony. *Mercury* decomposes the saturated aqueous solution, yielding cyanogen and bromide of mercury. (Löwig.)

Bromide of cyanogen dissolves without decomposition in oil of vitriol, hydrochloric acid, and nitric acid.

Combinations. Bromide of cyanogen unites with a small quantity of

Water, forming crystals, which remain solid at a higher temperature than the dry compound.—It is more soluble in water than the iodide. (Serullas.)—With Ammonia. (Bineau.)—More soluble than the iodide in *Alcohol*. (Serullas.)

Ammonio-bromide of Cyanogen.

a. *Liquid*. $6NH^3,CyBr$.—Bromide of cyanogen absorbs ammoniacal gas very rapidly at first, then more and more slowly, so that the complete saturation takes a very long time. The crystals of *b*, which form at first, are hereby converted into a colourless liquid, which smells strongly of ammonia, boils by the mere heat of the hand, and is quickly deprived of 4 At. ammonia, either by heat or by exposure to the air, being thereby converted into the following solid compound (Bineau):

b. *Solid*. $2NH^3,CyBr$.—Remains in the form of colourless needles, after the compound *a* has been exposed to the air, or as a white powder when *a* is heated to the boiling point. It is inodorous, has a very pungent taste, and is permanent in the air. Fuses below a *red heat*, giving off ammonia with ebullition, yielding a sublimate of hydrobromate of ammonia, and when heated to redness, leaves mellon:

$$3(2NH^3,C^2NBr) = 2NH^3 + 3NH^4Br + C^6N^4.$$

Nitric acid sets bromine free from it.—*Oil of vitriol* eliminates hydrobromic acid gas, mixed with vapours of bromine.—*Hydrochloric acid* dissolves it without evolution of gas.—*Water* dissolves it readily, forming a liquid which throws down bromide of silver from a silver-solution, but yet does not contain hydrobromate and cyanate of ammonia; for by evaporation it yields crystals, which, when heated to redness, leave mellon. (Bineau, *Ann. Chim. Phys.* 67, 239; 70, 257.)

(*a*). *Liquid.*			Bineau.	(*b*). *Solid.*			Bineau.
$6\ NH^3$	102	49·04	48·5	$2\ NH^3$	34	24·28	24·9
CyBr	106	50·96	51·5	CyBr	106	75·72	75·1
$6NH^3,CyBr$	208	100·00	100·0	$2NH^3,CyBr$	140	100·00	100·0

According to Cloez & Cannizzaro (*Compt. rend.* 32, 62), the substance just described is a mixture of hydrobromate of ammonia with *Cyanamide* Cy,H^2N (*vid.* p. 145).

Secondary Nucleus. C^2NCl.

Volatile Chloride of Cyanogen. C^2NCl.

BERTHOLLET. *Ann. Chim.* 1, 35.
GAY-LUSSAC. *Ann. Chim.* 95, 200; also *Schw.* 16, 55; also *Gilb.* 53, 168.
SERULLAS. *Ann. Chim. Phys.* 35, 291, and 337; also *N. Tr.* 16, 1, 213; abstr. *Pogg.* 11, 87.—*J. Chim. méd.* 7, 129; also *Pogg.* 21, 495.
WURTZ. *Compt. rend.* 24, 437; *Ann. Pharm.* 64, 307; *Jahresber.* 1847—8, 475.—Further and more fully: *Ann. Pharm.* 79, 280; *Jahresber.* 1851, 377.

Chlorure de Cyanogène gazeux; Protochlorure de Cyanogène; Flüssiges Chlorcyan. (Wurtz.)—Berthollet, by bringing chlorine in contact with hydrocyanic acid, obtained a peculiar substance, which he regarded as *oxidized prussic acid.* Gay-Lussac succeeded in preparing chloride of cyanogen in the state of gas, though mixed with carbonic acid, and examined many of its chemical relations. Serullas obtained it in the pure state, and investigated it more exactly. More recently Wurtz has obtained an extremely volatile liquid, having the same composition as the gas, and resembling it in most of its properties.

Formation.—1. By the action of chlorine gas on moist cyanide of mercury in the dark, and at a rather low temperature:

$$HgCy + 2Cl = HgCl + CyCl.$$

In about 8 hours the chlorine gas is completely converted into an equal volume of gaseous chloride of cyanogen. But by the action of light, or of a temperature of 30—40°, sal-ammoniac and traces of carbonic acid (and a yellow oil) are obtained, instead of chloride of cyanogen. The action of chlorine is accompanied by evolution of heat; if therefore the moist cyanide of mercury be introduced into bottles filled with chlorine, and containing more than 3 litres, the temperature may rise high enough to prevent the formation of chloride of cyanogen. (Serullas.) In the complete absence of water, chlorine gas does not act upon cyanide of mercury in the dark; but on exposure to light, a yellow oil is formed. (Gay-Lussac; Serullas.)—2. By passing chlorine through hydrated hydrocyanic acid. (Gay-Lussac.)

Preparation.—(a.) *Of the gas.*—Cyanide of mercury moistened with water, but not dissolved in it, is introduced into two bottles of a capacity not exceeding 3 litres, well closed with glass stoppers, and filled with chlorine gas, the proportion of cyanide of mercury being about 5 grammes to each litre of chlorine; the bottles are left for 24 hours in the dark, till in fact the chlorine has lost its yellow colour; then cooled by immersion in a mixture of ice and salt, producing a temperature at least as low as —18°, till the gaseous chloride of cyanogen solidifies in crystals; 100 grammes of water poured into each bottle; the resulting solution poured from all the bottles into a long-necked flask, which it must nearly fill; and this flask connected by a bent tube with a two-mouthed bottle containing chloride of calcium, so that the gaseous chloride of cyanogen may pass from its second mouth through a second bent tube into a bottle surrounded with a freezing mixture. If now the aqueous solution in the flask be warmed, the chloride of cyanogen collects in the crystalline form in the last bottle, which must then be closed very tight with a glass stopper. At ordinary temperatures, the crystals in the bottle melt, and are converted into gas. If however a small quantity of water be introduced into the bottle while it is immersed in the freezing mixture, and it be then taken out, still well closed, two layers are found in it, the upper of which is an aqueous solution of chloride of cynanogen, and the lower probably a hydrate of that compound. (Serullas.)

Methods of preparation formerly recommended by Serullas:—1. The same as above, excepting that the chlorine bottles contain only 1 litre. As soon as the chloride of cyanogen has condensed in the freezing mixture, chloride of calcium is introduced into each bottle to withdraw

the water, but in small quantities, so as not to cause any perceptible rise of temperature. The bottles, well closed, are then taken out of the freezing mixture; exposed for three days to a medium temperature, so that the gaseous chloride of cyanogen may be completely dehydrated; and again immersed in the freezing mixture, in which some bottles containing mercury are likewise immersed. As soon as the chloride of cyanogen is completely solidified, the bottles containing it are completely filled with the cooled mercury, in order to expel the air, and perhaps other foreign gases; they are then fitted, one after the other, with a gas-delivery tube; taken out of the freezing mixture, and heated by red-hot coals, held at some distance, because mere warming by the external air would be too slow. Violent ebullition then takes place; the air in the tube is first allowed to escape; and then the gaseous chloride of cyanogen is collected over mercury.—2. Since the solution of chloride of mercury obtained in preparing the above-mentioned yellow oil (oil of chloride of cyanogen) from aqueous cyanide of mercury and chlorine in sunshine, also contains chloride of cyanogen, that compound may be evolved from it in the gaseous state by heating the solution in a flask; the gas may then be passed through a tube containing chloride of calcium, marble, and chloride of calcium again, to free it from water and hydrochloric acid, and, lastly, through a tube bent downwards into a bottle surrounded with a freezing mixture, in which the gas solidifies in crystals. (Serullas.)

¶ Wöhler (*Ann. Pharm.* 73, 219) passes chlorine into a saturated solution of cyanide of mercury to which an excess of the salt in fine powder has been added, continuing the passage of the gas till the solution is completely saturated and the upper part of the vessel filled with the gas. The vessel is then closed and left in the dark, till after repeated agitation the whole of the chlorine is absorbed, or the whole of the cyanide of mercury dissolved. To removing any remaining excess of chlorine, the solution is shaken up with mercury. It is then heated in a flask, which is connected with a chloride of calcium tube and a conducting tube, and the gaseous chloride of cyanogen condensed, as in the process last described. ¶

The *extremely poisonous action of the gaseous chloride of cyanogen* renders it necessary in all these processes to take the greatest care to prevent its escape into the air and consequent inhalation. (Serullas.) [For this reason, a freezing mixture made with chloride of calcium is preferable to the ordinary mixture of ice and salt.]

Gay-Lussac passed chlorine gas through aqueous prussic acid, till it began to decolorize tincture of indigo; then removed the excess of chlorine by agitation with mercury; and evolved the gaseous chloride of cyanogen—which however was contaminated with carbonic acid—by moderately heating the solution.

¶ When chlorine gas is slowly passed into dilute hydrocyanic acid cooled to 0°, the liquid after a while separates into two layers, the lighter of which is a compound of chloride of cyanogen with hydrocyanic acid, 2CyCl,HCy. (p. 144.) If the stream of chlorine be too rapid, part of this product is carried over with it, and may be condensed in a receiver. From this compound the chloride of cyanogen may be obtained, by mixing it, after separation from the heavier stratum, with ice-cold water, and treating it with mercuric oxide, taking care to cool the vessel well, as otherwise the oxide may be reduced. Chloride of calcium is then added, the liquid distilled, and the vapour passed through a tube containing chloride of calcium into a flask cooled to 0°. The chloride of

cyanogen then condenses in the form of a colourless liquid, heavier than water. (Wurtz, *Ann. Pharm.* 79, 280.) ¶

Properties. The compound obtained by Serullas crystallizes at —18° in long transparent needles, sometimes united in hard, brittle masses. Between — 15° and — 12°, it melts to a transparent and colourless liquid, which retains its liquid form at + 20° under a pressure of 4 atmospheres, or when sealed up in a strong glass tube. But at ordinary temperatures it boils at — 12°. (Serullas.) — ¶. Wurtz's compound, on the contrary, crystallizes between — 5 and — 6°; and boils at + 15·5°; between those temperatures, it is a colourless, very mobile, and highly pungent liquid, heavier than water, and but slightly soluble therein. ¶ — The gas (which is colourless, according to Gay-Lussac) has an insupportable odour, excites a very copious flow of tears (likewise according to Gay-Lussac), and produces violent smarting on sore parts of the skin. Less than 1¼ grain given in the state of aqueous solution to a rabbit, kills it instantly. The gas and its aqueous solution are neutral to turmeric and litmus. (Serullas.) Gay-Lussac's gas reddens litmus, probably because it is contaminated with carbonic or hydrochloric acid.

				Wurtz.		Vol.	Density.
2 C	12·0	19·54		19·68	C-vapour	2	0·8320
N	14·0	22·80		22·24	N-gas	1	0·9706
Cl	35·4	57·66		57·72	Cl-gas	1	2·4543
C^2NCl	61·4	100·00		99·64		2	4·2569
						1	2·1284

Decompositions. 1. Volatile chloride of cyanogen changes spontaneously into fixed chloride of cyanogen. (Liebig, *Chim. org.* 1, 178.) — ¶ The liquid chloride of cyanogen obtained by Wurtz may be kept for years without alteration. If, however, an excess of chlorine be passed into dilute hydrocyanic acid, and the yellow liquid which separates be merely distilled, without previous washing or treatment with mercuric oxide, an impure product is obtained, which readily changes to the solid chloride; so likewise does the volatile chloride of cyanogen obtained by the action of chlorine on dry cyanide of mercury. But both these products, when washed with water, which removes the excess of chlorine, and perhaps also a small quantity of solid chloride of cyanogen, lose the property of changing to the solid compound. (Wurtz.) ¶ — 2. The gas mixed with oxygen cannot be set on fire by the electric spark, unless hydrogen be likewise added; in this case, a cloud is formed, with violent detonation and a bluish white light, 1 vol. gaseous chloride of cyanogen producing 1 vol. carbonic acid, and liberating ½ vol. nitrogen. (Gay-Lussac.) — 3. Moist gaseous chloride of cyanogen absorbed by aqueous potash, or aqueous solution of chloride of cyanogen mixed with potash, gives off a large quantity of carbonic acid on the addition of a stronger acid, and a solution is formed containing ammonia (Gay-Lussac, Serullas):

$$C^2NCl + 4HO = 2CO^2 + NH^3 + HCl.$$

4. Aqueous chloride of cyanogen, mixed, first with green vitriol, then with potash, and then with an acid, yields a green precipitate. (Gay-Lussac.) But this precipitate is not produced, if the potash be added first, then the iron-salt, and then the acid; hence the mere union with potash must produce a change in the compound, although no ammonia is thereby

formed. (Gay-Lussac, Serullas.) — 5. Two volumes of gaseous chloride of cyanogen passed over heated antimony, yield chloride of antimony and 1 vol. cyanogen gas. — 6. Potassium heated in the gas, emits a feeble light, absorbs a quantity of the gas equal in volume to the hydrogen which it would evolve in contact with water, and is converted into a dingy yellow mass, probably consisting of chloride and cyanide of potassium; inasmuch as its solution, when neutralized with nitric acid, yields a white precipitate with nitrate of silver, and forms prussian blue with iron-salts.

Combinations. — With *Water.* *a.* Chloride of cyanogen absorbs water of crystallization, and in the hydrated state remains solid at a higher temperature than when pure. (Serullas.) According to a more recent statement of Serullas, on the contrary, (*J. Chim. méd.* 7, 129), a small quantity of water forms with chloride of cyanogen a liquid hydrate (p. 142). — *b.* Chloride of cyanogen dissolves very readily in water, 1 vol. water at 20° and under the ordinary pressure absorbs 25 vol. of the gas. The solution may be kept without alteration, and when boiled, gives off the gas in its original state. (Serullas.) It does not precipitate silver-solution. (Gay-Lussac.) The liquid compound obtained by Wurtz is but sparingly soluble in water.

1 vol. alcohol at 20° absorbs very quickly 100 vol. gaseous chloride of cyanogen, and 1 vol. ether absorbs 50 vol. (Serullas.)

¶ Hydrocyanate of Chloride of Cyanogen. 2CyCl,HCy.— Formed by the action of chlorine on aqueous hydrocyanic acid.—*Preparation.* Chlorine gas is passed into cold dilute hydrocyanic acid contained in a retort, to the neck of which is adapted a tube bent at right angles, and passing into a receiver containing water cooled to 0°. Two liquids then collect in the receiver, the lower of which is watery, and the upper a liquid smelling strongly of chloride of cyanogen. The latter, which is the double chloride, may be separated by decantation, agitated with water at 0°, and then distilled over chloride of calcium. (Wurtz.)

Colourless liquid, lighter than water; solidifies only at the temperature of a mixture of solid carbonic acid and ether; boils at about 20°. Smells like chloride of cyanogen. It is inflammable, and burns in the air with a violet flame. (Wurtz.)

This liquid may be kept for years without exhibiting any change of colour or separation of crystals. In an atmosphere of chlorine, it is quickly converted into solid chloride of cyanogen, Cy^3Cl^3, which settles on the sides of the vessel in large, well-developed crystals. Bromine rapidly converts it into a semi-solid mass, which, when gently heated, gives off bromide of cyanogen, but at a higher temperature yields solid chloride of cyanogen. Mercuric oxide decomposes it, yielding liquid chloride of cyanogen (*vid. sup.*) (A. Wurtz, *Ann. Pharm.* 79, 280; abstr. *Jahresber.* 1851, 377.)

			Wurtz.	
6 C	36·0	24·01	23·0	24·1
H	1·0	0·66	0·6	0·9
2 Cl	70·8	47·31	46·0	49·1
3 N	42·0	28·02	27·9	28·0
2CyCl,HCy	149·8	100·00		

The differences in the analytical results show that the compound is not very stable. *(Wurtz.)*

AMMONIO-CHLORIDE OF CYANOGEN. — $2NH^3,C^2NCl$. In whatever proportion gaseous chloride of cyanogen and ammoniacal gas may be mixed, they always combine in the ratio of 1 vol. chloride of cyanogen to rather more than 2 vol. ammoniacal gas, and form white, inodorous, crystalline grains, which redden litmus. These crystals fuse when heated, give off ammonia with slight decrepitation, then sal-ammonia, and leave mellon:

$$3(2NH^3,C^2NCl) = 2\,NH^3 + 3NH^4Cl + C^6N^4.$$

rom the composition of this substance we might suppose that it would be decomposed by water, and form a solution of hydrochlorate and cyanate of ammonia; this, however, is not the case; for the solution, either in cold or in boiling water, exhibits neither the reactions of cyanate of ammonia nor those of urea, and leaves on evaporation a white crystalline mass, which, like the original compound, leaves mellon when heated. Oil of vitriol dissolves the compound rapidly, with evolution of hydrochloric acid gas free from carbonic acid; nitric acid dissolves it slowly, with evolution of carbonic and hydrochloric acid, together with small quantities of chlorine and hyponitric acid. Potash separates ammonia from it. Hydrochloric acid, whether in the gaseous state or dissolved in water, exerts no action upon it. (Bineau, *Ann Chim. Phys.* 67, 236; 70, 251.)

¶ *Cyanamide.* — Cy,NH^2. According to Cloez & Cannizzaro (*Compt. rend.* 32, 62; *Instit.* 1851, 18; *Ann. Pharm.* 78, 228; *Jahresber.* 1851, 382), the substance just described is a mixture of sal-ammoniac and an amide of cyanogen $C^2H^2N^2 = Cy,NH^2$:

$$CyCl + 2NH^3 = NH^4Cl + Cy,NH^2.$$

To obtain this amidogen-compound in the separate state, gaseous chloride of cyanogen is passed into a solution of ammoniacal gas in anhydrous ether; chloride of ammonium then separates out, and on distilling the filtrate in the water-bath, pure cyanamide remains behind. This compound is white, crystalline, melts at 40°, but may be kept in the fluid state at much lower temperatures; under these circumstances, however, it solidifies instantly on being touched with any solid body, such as a glass rod. At 150°, it suddenly assumes the solid form, with great evolution of heat. The solid body thus formed has the same composition as cyanamide; but its properties agree exactly with those of *Melamine*, which substance may therefore be regarded as an amide of cyanuric acid, *Cyanuramide*, or *Cyanuramine*, formed by the union of 3 At. cyanamide into one. — Cyanamide undergoes no alteration in dry air. It dissolves readily in water, but the solution, when evaporated, leaves a nearly insoluble residue, probably cyanuramide. Cyanamide dissolves without decomposition in alcohol and ether; alkalis decompose it. With some acids, nitric acid, for example, it forms crystallizable compounds. A small quantity of nitric acid added to an ethereal solution of cyanamide, forms nitrate of urea.

Chloride of cyanogen acts in a similar manner on the compound ammonias; thus, with methylamine, C^2H^5N, it forms *Cyanomethylamide*, Cy,C^2H^4N; with ethylamine, C^4H^7N: *Cyanethylamide*, Cy,C^4H^6N; and with amylamine, $C^{10}H^{13}N$: *Cyanamylamide*, $Cy,C^{10}H^{12}N$. A similar action is exerted by bromide and iodide of cyanogen. (Cloez & Cannizzaro.)

CHLORIDE OF CYANOGEN AND TITANUM. — $2FiCl^2,CyCl$. Gaseous chloride of cyanogen acts instantly and with great evolution of heat on bichloride of titanium, converting it into a bulky yellow, crystalline mass, which must be shaken up and heated gently, in order that it may be completely saturated with the chloride of cyanogen.

Lemon-yellow, very volatile; begins to volatilize considerably below 100°, subliming in clear lemon-yellow crystals, which appear to be rhombic octohedrons. It fumes very strongly in damp air, quickly becoming milk-white, and exhaling the odour of chloride of cyanogen. Water dissolves it, with great rise of temperature and evolution of chloride of cyanogen, forming a clear solution. It dissolves without alteration in warm bichloride of titanium, separating out again in crystals on cooling. It absorbs ammonia with great rise of temperature, forming with it an orange-red compound, which also turns white in moist air, and is decomposed by water, with partial separation of titanic acid. (Wöhler, *Ann. Pharm.* 73, 219; *Pogg.* 79, 397; *J. pr. Chem.* 50, 233; *Pharm. Centr.* 1850, 81; *N. Ann. Chim. Phys.* 29, 182; *Instit.* 1850; *Jahresber.* 1849, 266; 1850, 355.)

			Wöhler.
$2\ TiCl^2$	189·6	75·54	75·89
$CyCl$	61·4	24·46	
$2TiCl^2,CyCl$	251·0	100·00	

Chloride of cyanogen does not appear to form a similar compound with bichloride of tin. (Wöhler.)

CHLORIDE OF CYANOGEN AND ANTIMONY. — $SbCl^5,CyCl$. When gaseous chloride of cyanogen is passed over pentachloride of antimony, the latter becomes slightly heated, turbid, and gradually filled with delicate crystals. After saturation, the compound forms a white crystalline mass. When heated, only a portion of it sublimes undecomposed, the greater part giving up its chloride of cyanogen. Water decomposes it instantly. — It absorbs ammonia, with rise of temperature, forming a yellow, pulverulent body. (L. Klein, *Ann. Pharm.* 74, 87.)

			Klein.
$SbCl^5$	306·0	83·29	85·94
$CyCl$	61·4	16·71	14·06
$SbCl^5,CyCl$	367·4	100·00	100·00

2·785 grm. pentachloride of antimony absorbed 0·466 grm. chloride of cyanogen, corresponding to 14·06 p. c. The saturation was doubtless incomplete. (Klein.)

CHLORIDE OF CYANOGEN AND IRON. — $FeCl^2,CyCl^2$. Sublimed sesquichloride of iron absorbs gaseous chloride of cyanogen, with evolution of heat, fusing with it into a black mass; the compound was not, however, obtained in a complete state of saturation. When heated, it fuses, swells up, and gives off gaseous chloride of cyanogen;—it is remarkable, however, that this decomposition likewise yields solid chloride of cyanogen sublimed in crystals. (Klein.) ¶

Doubtful Compounds.

Cyanide of Phosphorus.

a. Cyanogen liquefied by strong pressure dissolves phosphorus in a few days, probably converting it into cyanide of phosphorus. (Kemp.)

b. When 5 grains of phosphorus are carefully heated with 20 grains of cyanide of mercury, at the closed end of a glass tube, the other end of which is connected with a small receiver, there is often formed—unless a dangerous explosion takes place—a white sublimate having a very pungent odour of phosphorus and cyanogen; it evaporates for the most part in the air, reddens litmus strongly when moist but not when dry, and dissolves completely in phosphoric and hydrocyanic acid. This body may be supersaturated with an indefinite quantity of phosphorus, and forms with it a yellowish white powder, which takes fire spontaneously in the air, burning with a dazzling greenish white flame, a kind of detonation, and an odour of phosphorus and hydrocyanic acid. — Cyanide of phosphorus dissolves in water with ebullition and separation of finely divided phosphorus, forming a solution of phosphoric acid, with traces of hydrocyanic acid. It unites with potassium without any particular phenomenon, and the compound dissolves in water with evolution of phosphuretted hydrogen, forming a solution of phosphate and hydrocyanate of potash (Cenedella, *J. Pharm.* 21, 683; also *Ann. Pharm.* 18, 70).

Cyanide of Nitrogen?

When a moderately concentrated aqueous solution of cyanide of potassium is added drop by drop to chloride of nitrogen placed under a layer of water, the chloride of nitrogen loses its yellow colour, decrepitates slightly, and rapidly gives off gas-bubbles, which soon fill the vessels with a thick white fume. A piece of phosphorus placed in the way of the bubbles as they rise, or of the fumes, causes a fiery explosion which bursts the vessel. If we endeavour to collect the gas by means of a gas-delivery tube, we obtain nothing but nitrogen, the gas being decomposed by the water; hence nothing but bubbles of nitrogen is obtained, and no white fumes, if the solution of cyanide of potassium be too dilute; but if the solution be too strong, or if pieces of solid cyanide of potassium be used, explosion takes place. (Millon. *Ann. Chim. Phys.* 69, 76.) — The explosion of cyanide of nitrogen is most tremendous. (Marchand, *J. pr. Chem.* 19, 5.) — Berzelius (*Lehrb.*) suggests that the explosion may be due to undecomposed chloride of nitrogen.

Cyanoform. C^2HCy^3. ?

Acetate of lime carefully distilled with an equal weight of
blue or cyanide of mercury, yields neither acetone, nor acet
hydrocyanic acid, but a neutral distillate consisting of c
water, from which pure cyanoform may be obtained by r
chloride of calcium. — Cyanoform is a colourless, toler
tral liquid, which smells like hydrocyanic acid and tob

take fire by contact with the flame of a candle, and dissolves in water, alcohol, and ether. (Bonnet, *Institut*, 1837, No. 196, 47; also *J. pr. Chem.* 10, 207.) — That this compound is cyanoform is a mere supposition of Bonnet's; such a compound ought to be inflammable. It therefore deserves further examination.

¶ Addenda.

Compounds of Hydrocyanic Acid with Metallic Chlorides.

Hydrocyanate of Titanic Chloride. — $TiCl^2,HCy$. When anhydrous prussic acid is poured into bichloride of titanium, combination takes place, attended with rise of temperature and ebullition (on which account the substances must be cooled to 0° before mixing, or the hydrocyanic acid must be passed in the form of gas into the titanic chloride), and formation of a yellow pulverulent mass; the excess of prussic acid is then distilled off, and the compound sublimed by careful heating. It is very volatile, subliming below 100°, in the form of clear, shining, lemon-yellow crystals (rhombic pyramids and combinations thereof), which if rapidly sublimed, unite into a coherent mass. It fumes slightly in the air, smells strongly of hydrocyanic acid, quickly turns white, and deliquesces to a clear viscid solution. Water dissolves it, with rise of temperature, and forms a clear solution; if the quantity of water be small, gaseous hydrocyanic acid is given off as the substance dissolves. It is not altered by sublimation in chlorine gas. When its vapour is passed through a red-hot glass tube, it covers the tube with copper-coloured nitride of titanium mixed with charcoal. (Wöhler, *Ann. Pharm.* 73, 226.)

			Wöhler.
$TiCl^2$	94·8	77·86	77·67
HCy	27·0	22·14	
$TiCl^2,HCy$	121·8	100·00	

Hydrocyanate of Antimonic Chloride. — $SbCl^5,3HCy$. When the vapour of anhydrous prussic acid is brought in contact with pentachloride of antimony, heated to 30°, this compound is produced in the form of clear definite prisms, which volatilize between 70° and 100°, but at the same time undergo partial decomposition, even in an atmosphere of carbonic acid. The compound is deliquescent; does not fume in the air; is decomposed by water, with separation of antimonic acid, and unites with ammonia, forming a brown-red, pulverulent mass. (Klein, *Ann. Pharm.* 74, 86.)

			Klein.
$SbCl^5$	306	79·07	77·74
3 HCy	81	20·93	
$SbCl^5,3HCy$	387	100·00	

quich
of heat, cyanate of Stannic Chloride.—$SnCl^2,HCy$. ? Bichloride of tin
ever, obtain anhydrous prussic acid, without sensible rise of temperature,
swells up, and lid crystalline body; if the acid in the gaseous state be
however, that t a tube in which the stannic chloride is placed, so as
gen sublimed in c e surface, the compound is obtained in fine crystals.
colourless, refract light strongly, and appear to be

isomorphous with the corresponding titanium-compound. In a stream of dry air, they volatalize as quickly as anhydrous prussic acid, becoming at the same time white and opaque. They are decomposed by water and by damp air. They unite with ammoniacal gas, forming a white substance which may be sublimed. No analysis was made of this compound, on account of its great volatility; but it appears to be analogous to the titanium-compound (p. 148). (Klein, *Ann. Pharm.* 74, 85.)

Hydrocyanate of Ferric Chloride.—$Fe^2Cl^3,2HCy$. Sublimed ferric chloride and anhydrous prussic acid unite, with a hissing noise, and form a brown-red liquid, which soon solidifies in the crystalline state. The compound deliquesces in the air, giving off hydrocyanic acid; melts at 100°; and unites with ammonia, forming a greenish black powder which dissolves in water with separation of prussian blue, and therefore contains protochloride of iron. The compound, when heated, yields ferruginous sal-ammoniac, hydrocyanic acid, and protochloride of iron. (Klein, *Ann. Pharm.* 74, 87.)

				Klein.
Fe^2Cl^3	162·2	....	75·04	74·23
2 HCy	54·0	....	24·96	
$Fe^2Cl^3,2HCy$	216·2	....	100·00	¶

COMPOUNDS CONTAINING 4 AT. CARBON.

KLUMENE SERIES.

A. Primary Series.

Primary Nucleus. Klumene. C^4H^2.

Edm. Davy. *Records of gen. Sc.* Nov. 1836; also *Ann. Pharm.* 23, 144; also *J. Pharm.* 23, 143.

The word *Klumene* is formed from the letters of the word Kalium, because the primary nucleus is obtained from a potassium-compound. An atom of this nucleus may be supposed to contain 4 At. C arranged in a square, with the 2 At. H in the middle, one above and one below.

The black mass which often passes over with the potassium, in the preparation of that metal from burnt tartar and charcoal (III, 8), and appears to be a carbide of potassium, gives off, when immersed in water, a peculiar combustible gas, which is klumene gas.

					Vol.	Density.
4 C	24	92·31		C-vapour	4	1·6640
2 H	2	7·69		H-gas	2	0·1386
C^4H^2	26	100·00		Klumene-gas	2	1·8026
					1	0·9013

This gas is very inflammable, and burns in the air with a flame as bright as that of olefiant gas. 2 volumes of it mixed in a tube with excess of oxygen, and inflamed by the electric spark, consume 5 vol. oxygen, and produce, with violent explosion, 4 vol. carbonic acid gas, together with water. The 4 vol. carbon vapour in the 2 vol. of the gas consume 4 vol. oxygen, and form 4 vol. carbonic acid gas; and the 2 vol. hydrogen with 1 vol. oxygen form water. The gas, when mixed with chlorine, takes fire spontaneously, even in the dark, the combustion being attended with explosion, a red flame, and deposition of charcoal.

Water absorbs its own volume of this gas, and gives it up again unchanged on being heated. (E. Davy.)

Maleic Acid. $C^4H^2O^4$.

LASSAIGNE. *Ann. Chim. Phys.* 11, 93; also *N. Tr.* 4, 2, 231.
PELOUZE. *Ann. Chim. Phys.* 56, 72; also *Pogg.* 36, 53; also *Ann. Pharm.* 11, 263; also *J. pr. Chem.* 3, 26.
LIEBIG. *Ann. Pharm.* 11, 276.
REGNAULT. *Ann. Chim. Phys.* 62, 208; also *Ann. Pharm.* 19, 145.
BRACONNOT. *Ann. Chim. Phys.* 39, 10; also *N. Tr.* 18, 2, 243.
PH. BUCHNER. *Ann. Pharm.* 49, 57.

Pyromalic acid, Equisetic acid, Maleinsäure, Brenzliche Aepfelsäure, Brenzäpfelsäure, brenzliche Vogelbeersäure, Acide maleique, Acide pyromalique, Acide pyrosorbique, Acide equisetique. — Vauquelin (*Ann. Chim. Phys.* 6, 337; also *Schw.* 24, 162) and Braconnot (*Ann. Chim. Phys.* 8, 149; also *N. Tr.* 3, 1, 144) obtained, by the dry distillation of malic acid, first an acid aqueous distillate, and then a needle-shaped sublimate. Lassaigne, in 1819, showed that the distillate contained a peculiar acid (Pyromalic acid, or, according to Pelouze, Maleic acid), and that the needles consist of another acid, viz., Fumaric acid. Braconnot, in 1828, discovered Equisetic acid in *Equisetum fluviatile*, and Regnault showed that this acid is identical with maleic acid. — ¶ Liebig, however, (*Handb. d. Org. Chem.* 272) considers the acid of *Equisetum fluviatile* as identical, not with maleic, but with Aconitic acid, the acid of *Aconitum Napellus;* and this opinion has been confirmed by Baup, who has lately (*Ann. Pharm.* 77, 293) examined these acids more fully. (*Vid. inf.*) ¶

Sources. In *Equisetum fluviatile* and *E. limosum* [?] in combination with magnesia, potash, and lime.

Formation. By the dry distillation of malic acid (VII, 81) at 200°. (Pelouze.)

Preparation. 1. *From Equisetum?—a.* The recently expressed and filtered juice of *Equisetum fluviatile* is evaporated to a syrup; the syrup boiled with alcohol; the portion insoluble in alcohol dissolved in water; the phosphoric acid present in the aqueous solution precipitated by acetate of baryta; and afterwards the maleic acid by subacetate of lead. The latter precipitate, decomposed by an equivalent quantity of dilute sulphuric acid, yields an acid filtrate which crystallizes completely when evaporated to a syrup. On dissolving the crystalline mass in alcohol, sulphate and phosphate of lime remain behind; and the filtrate, after evaporation and cooling, yields crystals which still retain small quantities of phosphoric acid and a brownish substance. To remove these impurities, the aqueous solution is precipitated by nitrate of lead; the liquid filtered from the slight brownish precipitate, and then precipitated with subacetate of lead; the resulting precipitate washed, suspended in water, and decomposed by a stream of sulphuretted hydrogen; the liquid filtered from the sulphide of lead, which retains the brown colouring matter, and finally evaporated till it crystallizes. (Braconnot.) — *b.* The stems of *Equisetum limosum* in the flowering state are cut up, and bruised with water; the juice pressed out, heated to the boiling point, filtered from coagulated vegetable albumen; the clear, slightly acid filtrate neutralized with carbonate of soda; the phosphoric and sulphuric acid precipitated by

acetate of baryta; the filtrate mixed with a slight excess of neutral acetate of lead; the copious yellowish precipitate of maleate of lead washed, suspended in water, and decomposed by sulphuretted hydrogen; the acid filtrate decolorized by digestion with animal charcoal; the liquid again filtered, heated with carbonate of lime, and then mixed with carbonate of ammonia, whereby the rest of the phosphoric acid is thrown down, together with carbonate of lime; the filtrate containing the maleate of ammonia precipitated by neutral acetate of lead; the precipitate again decomposed by sulphuretted hydrogen; the colourless filtrate evaporated to the crystallizing yoint; the crystalline mass dissolved in ether, which leaves acid equisetate of magnesia undissolved, but quickly dissolves the acid; the ethereal filtrate evaporated to dryness; the residue dissolved in a small quantity of water, and the solution left to evaporate in vacuo till it crystallizes. (Regnault.) — ¶ According to Liebig and Baup (*vid. sup.*) the acid of the equisetum is not maleic, but aconitic acid, and differs from maleic acid in several respects; thus, maleic acid is volatile, equisetic acid not; the former yields with potash a quadro-acid salt, which the latter does not; the two acids also differ in solubility and crystalline form. The observations of Dessaignes (*Compt. rend.* 31, 432) likewise tend to the same conclusion. ¶

2. *By the dry distillation of Malic acid.* — Malic acid is heated in a capacious retort at a temperature quickly rising to 200°. The acid is contained in the watery liquid which first passes over, and crystallizes when that liquid is evaporated and cooled. (Lassaigne, Pelouze.) If the distillation takes place under 200°, the chief product is fumaric acid. The maleic acid does not separate from the distillate till that liquid has been evaporated to a syrupy consistence. (Pelouze.)

Properties. Long colourless prisms (Lassaigne); rhomboidal prisms (Pelouze); oblique rhombic prisms, with octohedral faces (Büchner); needles united in radiated masses (Braconnot, Regnault). Effloresces strongly when its aqueous solution is abandoned to spontaneous evaporation. (Büchner.) Melts at 47·5°, and on cooling solidifies in a radiated nacreous mass; at a higher temperature, it sublimes in long slender needles. (Lassaigne.) Melts at 30°, boils at 160°, and sublimes for the most part unaltered. (Pelouze.) Tastes very sour, and produces a very unpleasant after-taste (Pelouze, Regnault); tastes very sour, and afterwards irritating, astringent, and metallic. (Büchner.) Reddens litmus strongly. Permanent in the air.

	Crystallized.		Pelouze.	Liebig.	Regnault.
4 C	24	41·38	41·31	41·44	41·34
2 H	2	3·45	3·50	3·50	4·04
4 O	32	55·17	55·19	55·06	54·62
$C^4H^2O^4$	58	100·00	100·00	100·00	100·00

Büchner regards maleic acid as bibasic $= C^8H^4O^8 = 2HO, C^8H^2O^6$, a supposition which is certainly favoured by the tendency of this acid to form acid salts.

Decompositions. 1. Maleic acid, when heated partly, volatilizes unchanged, and without leaving any residue of charcoal, and is partly converted, without loss of water, into fumaric acid, $C^8H^4O^8$, which is polymeric with it, and partly, with loss of water, into fumaric anhydride $C^8H^2O^6$:

$$2C^4H^2O^4 = C^8H^4O^8; \text{ and } 2C^4H^2O^4 = 2HO + C^8H^2O^6.$$

Pelouze regards this anhydride as C^4HO^3. — Maleic acid, when suddenly heated to 160° in a retort, whose neck is sharply inclined downwards, so that the condensed vapours cannot flow back again, distils over for the most part unchanged, only a few crystals of fumaric acid remaining in the retort. If the acid be kept for some time at a temperature but little above its melting point, it gradually solidifies in the form of crystallized fumaric acid, which will then sustain a heat of 200° without melting. The transformation takes place more quickly when the maleic acid is boiled in a long narrow glass tube, either open or closed, in which the vapours as they condense continually flow back again. Fumaric anhydride is produced when the maleic acid is repeatedly distilled, and the watery distillate which first passes over continually removed. (Pelouze.) [Under these circumstances fumaric acid appears to be first produced, and afterwards to be converted into the anhydride.] — ¶ 2. Maleic acid fermented under the influence of casein is converted into succinic acid. (Vid. *Maleate* of *Lime*.) ¶

Combinations. Maleic acid dissolves in about 1 pt. of cold water (Pelouze); in 2 pts. of water at 10°. (Lassaigne.) The solution, when evaporated in the air, yields copious crystalline effloresences (Pelouze), and when evaporated by the aid of heat, becomes covered with crystalline crusts. (Braconnot.)

The *Salts of Maleic acid*, the *Maleates*, are all soluble in water, excepting the neutral lead, copper, and silver salts; hence normal alkaline maleates precipitate the salts of these metals. The bimaleates of ammonia, potash, and soda, are less soluble in water than the monomaleates; the contrary is, however, the case with the other bases which are capable of forming bi-acid salts with this acid.

Maleate of Ammonia. — *a. Monomaleate.* The aqueous solution of the acid supersaturated with ammonia leaves a crystalline jelly when evaporated over lime in vacuo. Absolute alcohol added to the concentrated aqueous solution throws down the salt in the form of a white crystalline powder, which may be dried by repeated washing with alcohol, and pressing between paper, but when exposed to the air, quickly becomes glutinous and deliquescent. (Buchner.) — ¶ This salt does not precipitate a solution of sesquichloride of iron, a character which distinguishes it from the corresponding salt of aconitic acid. (Dessaigne.) ¶

b. Bimaleate. Obtained by exactly neutralizing a known quantity of the aqueous acid with ammonia, then adding an equal quantity of the acid, and evaporating to the crystallizing point at a gentle heat. Crystalline laminæ, which are permanent in the air, redden litmus, and give off nothing at 100°; their solution evolves ammonia when boiled. Very easily soluble in water, but not in alcohol.

Pelouze and Braconnot (the latter with the acid from *Equisetum*), likewise obtained a crystallizable ammoniacal salt, but do not state whether it was neutral or acid. Regnault, however, obtained from the acid of *Equisetum*, by supersaturation with ammonia and evaporation in vacuo over oil of vitriol, merely a slightly acid syrup, but no crystals.

Crystallized.			Büchner.	Or:			Büchner.
8 C	48	36·09	36·36	NH^3	17	12·78	12·70
N	14	10·53	10·46	$2C^4H^2O^4$	116	87·22	
7 H	7	5·26	5·16				
8 O	64	48·12	48·02				
$NH^3,2C^4H^2O^4$	133	100·00	100·00				100·00

¶ Bimaleate of ammonia yields, by dry distillation, a substance — similar to that which is obtained under like circumstances from acid malate of ammonia — which, when subjected to the continued action of hydrochloric acid, is converted into aspartic acid. The acid obtained from *Aconitum* or *Equisetum* does not yield aspartic acid when similarly treated. (Dessaignes.) ¶

Maleate of Potash. — *a. Normal.* An aqueous solution of carbonate of potash, neutralized while hot with the acid, and evaporated to a syrup, yields a few soft radiated crystals; from the concentrated aqueous solution, absolute alcohol throws down a white, closely aggregated crystalline powder, which, after frequent washing with absolute alcohol, becomes granular from loss of water. It rapidly absorbs moisture, and dissolves very readily in water (Büchner). The salt crystallizes in fern-like tufts, and is somewhat deliquescent (Lassaigne); it crystallizes readily, and is very soluble in water (Pelouze); the salt obtained with the acid of *Equisetum* is very deliquescent, not crystallizable, and insoluble in alcohol. (Braconnot.)

Dried at 100°.			Büchner.	Or:			Büchner.
4 C	24·0	24·95		KO	47·2	49·06	48·84
H	1·0	1·04		C^4HO^3	49·0	50·94	
K	39·2	40·75	40·56				
4 O	32·0	33·26					
C^4HKO^4	96·2	100·00			96·2	100·00	

b. The *acid-salt* may be prepared like the acid ammoniacal salt, by means of carbonate of potash. From a mixture of the concentrated aqueous solution of the neutral salt with free maleic acid it does not separate till after some time. Small crystals, which redden litmus, and do not give off any water at 100°. They dissolve readily in water, but not in alcohol, which likewise does not withdraw any acid. (Büchner.)

	Crystallized.		Büchner.
KO	47·2	28·92	28·85
$2\ C^4H^2O^4$	116·0	71·08	
$C^4HKO^4, C^4H^2O^4 + Aq$	163·2	100·00	

According to Baup, maleic acid forms also a quadro-acid salt with potash; but aconitic acid does not.

No *Maleate of Potash and Ammonia* or *Maleate of Soda and Ammonia* appears to exist, at least in the solid state. (Büchner.)

Maleate of Soda. — *a. Normal.* Maleic acid neutralized hot with carbonate of soda, and afterwards evaporated and cooled, gradually solidifies to a crystalline jelly, consisting of small needles. If the concentrated solution be precipitated with absolute alcohol, and the precipitate left for some time in contact with absolute alcohol, which withdraws the water, there remains a white, crystallo-granular, easily pulverizable mass, which may be dried between paper; it does not absorb moisture from the air. (Büchner.) According to Pelouze, the salt is easily crystallizable, and dissolves readily in water.

	Dried at 100°.		Büchner.
NaO	31·2	38·90	37·01
C^4HO^3	49·0	61·10	
C^4HNaO^4	80·2	100·00	

Büchner prefers the formula $2NaO, C^8H^2O^6 + Aq$, which corresponds more nearly with his analysis.

b. Bimaleate. — 1. A certain quantity of maleic acid neutralized while warm with carbonate of soda, then mixed with another equal quantity of acid, and slowly evaporated, yields rhombic crystals. — 2. A concentrated solution of maleic or acetic acid added to a saturated solution of the mono-acid salt, throws down a crystalline precipitate of the bi-acid salt; if the solution be much diluted, the precipitate does not appear for some time, but is more distinctly crystallized. The crystals redden litmus strongly, dissolve very sparingly in cold water, more abundantly in boiling water; but are insoluble in alcohol, which, indeed, precipitates the salt from its aqueous solution. At 100°, the crystals give off their their water of crystallization, amounting to 28·32 per cent. (6 At.)

	Dried at 100°.		Büchner.
8 C	48·0	34·73	35·16
3 H	3·0	2·17	2·29
Na	23·2	16·79	16·67
8 O	64·0	46·31	45·88
$C^4HNaO^4,C^4H^2O^4$	138·2	100·00	100·00

Maleate of Potash and Soda? — On neutralizing an aqueous solution of maleate of soda with carbonate of potash, then evaporating and cooling the syrup, a few small crystals are obtained, floating in a gelatinous mother-liquid. On precipitating the concentrated aqueous solution with absolute alcohol, and setting the crystalline magma aside in contact with absolute alcohol, there is finally obtained a white, easily deliquescent crystalline powder, which gives off 9·13 p. c. (2 At.) water at 100°, and contains 25·55 p. c. potash and 17·64 p. c. soda. (Büchner.) [The precipitate is, perhaps, a mere mixture of the monomaleates of potash and soda.]

Maleate of Baryta. — *a. Monomaleate.* 1. Maleic acid forms with baryta-water a pulverulent precipitate, which disappears on the addition of a small quantity of cold water, but reappears after a while in shining scales. (Lassaigne.) The precipitate is converted into the crystalline scales, even without addition of water. (Pelouze.) On adding a saturated solution of baryta-water to the concentrated aqueous acid, the precipitate redissolves at first in the excess of acid; even when sufficient baryta-water has been added to neutralize the acid, the precipitate is but small; but after a few minutes, the whole solidifies to a tremulous gelatinous mass, resembling hydrate of alumina, which, after being pressed, dries up to small crystalline laminæ. These crystals are obtained still more distinct on evaporating the aqueous solution. (Regnault.) — 2. The salt is also obtained by adding carbonate of baryta to the hot aqueous acid, as long as effervescence continues, then filtering hot, and leaving the solution to crystallize. (Büchner.) — 3. The concentrated acid added to acetate of baryta, throws down a white crystallo-granular, neutral salt. Part of the salt, however, remains dissolved in the acetic acid which is set free, and may be precipitated by ammonia; this portion is also crystallo-granular, and has the same composition. (Büchner.) The salt crystallizes from its aqueous solution on cooling, in small shining needles united in stellate groups; and the solution, when evaporated at a temperature below its boiling point, becomes covered with a crystalline crust. (Büchner.) The crystals, after drying in the air, lose 5·62 p. c. (1 At.) of water at 100° (Büchner), and 7·3 per cent. at 150°. (Regnault.) They dissolve sparingly in cold water (in 9 pts. water at 20°, according to Regnault), with tolerable facility in boiling water, easily in aqueous maleic or acetic acid (Büchner); also in excess of baryta-water. (Pelouze.)

Dried at 150°.			Büchner.	*Dried at* 150°.			Büchner.
BaO	76·6	60·99	59·95	BaO	76·6	56·91	57·22
C^4HO^3	49·0	39·01		C^4HO^3	49·0	36·40	
				Aq	9·0	6·69	
C^4HBaO^4	125·6	100·00		+ Aq	134·6	100·00	

Crystallized.

BaO	76·6	53·34
C^4HO^3	49·0	34·12
2 Aq	18·0	12·54
$C^4HBaO^7 + 2$ Aq	143·6	100·00

According to Lassaigne, the salt contains 64·93 p. c. baryta.

b. Bimaleate. — 1. Obtained by saturating the aqueous acid with the salt *a.* — 2. By saturating a known quantity of the boiling aqueous acid with carbonate of baryta, and adding to the hot filtrate another equal quantity of the acid. The solution thus obtained yields, after tolerably strong concentration, indistinct crystals which redden litmus, give off 19·67° p. c. (5 At.) water of crystallization at 100°, and dissolve in water, but not in alcohol. (Büchner.)

Dried at 100°.			Büchner.
BaO	76·6	41·72	41·36
2 C^4HO^3	98·0	53·38	
HO	9·0	4·90	
$C^4HBaO^4,C^4H^2O^4$	183·6	100·00	

Maleate of Strontia. — *a. Monomaleate.* The aqueous acid, saturated at a boiling heat with carbonate of strontia and filtered, yields, by evaporation at a rather high temperature and subsequently cooling, fine silky needles. These needles do not in many cases make their appearance, even after the concentrated solution has been left standing for some time; but on stirring it, they separate almost instantly. (Büchner.)

Dried at 100°.			Büchner.	*Crystallized.*			Büchner.
SrO	52	47·27	46·60	SrO	52	35·62	
$C^4H^2O^4$	58	52·73		$C^4H^2O^4$	58	39·72	
				4 Aq	36	24·66	24·72
C^4HSrO^4,Aq	110	100·00		+ 5 Aq	146	100·00	

b. Bimaleate. — Prepared like the baryta-salt. Crystallizes very readily in very small transparent and colourless, rectangular prisms, which redden litmus strongly, give off 31·4 p. c. (8 At.) water at 100°; and dissolve in water, but not in alcohol. (Büchner.)

Dried at 100°.			Büchner.	*Crystallized.*			Büchner.
SrO	52	32·70	32·28	SrO	52	22·51	
C^4HO^3	49	30·82		C^4HO^3	49	21·21	
$C^4H^2O^4$	58	36·48		$C^4H^2O^4$	58	25·11	
				8 Aq	72	31·17	31·40
$C^4HSrO^4,C^4H^2O^4$	159	100·00		+ 8 Aq	231	100·00	

Maleate of Lime. — *a. Monomaleate.* The acid does not precipitate lime-water (Lassaigne); an aqueous mixture of maleate of potash and

chloride of calcium remains clear, but after a few days deposits needles which are but sparingly soluble in water. (Pelouze.) By saturating the boiling acid with carbonate of lime and evaporating the filtrate at a gentle heat, small needles are obtained united in saline crusts; they give off no water at 100°; dissolve readily in water, but not in alcohol. (Büchner.)

Crystallized, dried at 100°.			Büchner.
CaO	28	32·56	32·81
$C^4H^2O^4$	58	67·44	
C^4HCaO^4,Aq	86	100·00	

This salt, when fermented with casein, is converted into succinate of lime. (Dessaignes.)

b. Bimaleate. Formed by dissolving the salt *a* in a quantity of the aqueous acid equal to that which it already contains, and concentrating the solution somewhat strongly. Long rhombic prisms, which are permanent in the air, redden litmus, give off 24·1 p. c. (5 At.) of water at 100°, and dissolve readily in water, but not in alcohol. Oxalic acid added to the solution, throws down the lime. (Büchner.)

Dried at 100°.				*Crystallized.*			Büchner.
CaO	28	20·74	20·88				
C^4HO^3	49	36·30		135	75		
$C^4H^2O^4$	58	42·96					
				5 Aq	45	25	24·1
$C^4HCaO^4,C^4H^2O^4$	135	100·00		+5 Aq	180	100	

Maleate of Magnesia. — a. Monomaleate. The aqueous acid boiled with excess of carbonate of magnesia, then filtered and evaporated to a small bulk, deposits merely a few flakes; when evaporated to dryness, it leaves a tumefied spungy mass, which dissolves readily, even in a very small quantity of water. By precipitating the concentrated solution with absolute alcohol, and repeatedly wetting the gummy precipitate with that liquid, there is obtained a white, bulky, non-hygroscopic powder, which gives off 27·26 p. c. water at 100°, dissolves very readily in water, and likewise in aqueous alcohol. (Büchner.)

Dried at 100°.			Büchner.
MgO	20	25·64	26·24
$C^4H^2O^4$	58	74·36	
C^4HMgO^4,HO	78	100·00	

b. Bimaleate. By cooling a solution of 1 At. of the salt *a* and 1 At. maleic acid in hot water, small transparent and colourless rhombic crystals are obtained, which redden litmus strongly, grate between the teeth, taste like Epsom salts, and dissolve readily in water, but are insoluble in alcohol. At 100°, they give off 34·95 p. c. (5 At.) water; so that $MgO,C^8H^2O^6$ remains behind. (Büchner). [Can it be that at this temperature 2 At. of the salt are resolved into 2 At. of the mono-acid salt and 1 At. fumaric anhydride?

$$2(C^4HMgO^4,C^4H^2O^4) = 2C^4HMgO^4 + C^8H^2O^6 + 2HO]$$

Dried at 100°.			Büchner.
MgO	20	16·95	17·33
$C^8H^2O^6$	98	83·05	
	118	100·00	

Crystallized.			Büchner.
MgO	20	11·05	11·37
$C^8H^2O^6$	98	54·14	
7 Aq	63	34·81	34·95
$C^4HMgO^4,C^4H^2O^4+6Aq$	181	100·00	

Maleate of Zinc. — The aqueous acid boiled with excess of carbonate of zinc, then filtered and gently evaporated, deposits the salt in light gelatinous flakes, which become quite crystalline on standing; on heating the solution, the salt separates in crystalline crusts. The crystals give off nothing at 100°; they are perfectly neutral, and dissolve readily in water, but are insoluble in alcohol. (Büchner.)

Crystallized.			Büchner.
ZnO	40	37·38	37·42
C^4HO^3	49	45·80	
2 Aq	18	16·82	
C^4HZnO^4+2Aq	107	100·00	

The salts of equisetic acid precipitate protochloride of *tin*. (Braconnot.)

Maleate of Lead. — 1. Free maleic acid forms a precipitate with neutral acetate of lead (Lassaigne), but not with the nitrate (Braconnot); if the solution is dilute, the white precipitate changes in a few minutes into shining micaceous laminæ; but if the solution is concentrated, and the acetate of lead in excess, the mixture solidifies to a tremulous mass, which changes slowly — or quickly on the addition of water — into crystalline laminæ, which with difficulty give off their 16·5 p. c. (3 At.) water. (Pelouze.) — 2. Maleate of potash added to nitrate of lead, throws down white flakes; these soon change to a translucent pasty mass, and then, when washed upon a filter, diminish considerably in volume, and are converted into small pearly needles. (Lassaigne.) The salt dissolves in nitric, but not in acetic acid. (Braconnot.)

Dried at 100°.				*Crystallized.*			Pelouze.
PbO	112	69·56	69·05	PbO	112	59·58	
4 C	24	14·91	15·20	C^4HO^3	49	26·06	
H	1	0·62	0·70	3 Aq	27	14·36	16·5
3 O	24	14·91	15·05				
C^4HPbO^4	161	100·00	100·00	+3 Aq	188	100·00	

Ferric Maleate. — Neither the free acid nor the potash-salt precipitates ferric acetate; the boiling acid dissolves but a very small quantity of ferric hydrate, and the brownish solution yields on evaporation a brown-red greasy residue. (Büchner.)

Maleate of Nickel. — By boiling the aqueous acid with carbonate of nickel, and evaporating the dark green, slightly acid filtrate, a gummy liquid is obtained, and ultimately apple-green crystals and crystalline crusts, insoluble in alcohol, but readily soluble in water. (Büchner.)

Dried at 100°.			Büchner.
NiO	37·5	39·27	39·06
$C^4H^2O^4$	58·0	60·73	
C^4HNiO^4+Aq	95·5	100·00	

Maleate of Copper. — 1. A dilute solution of an alkaline equisetate precipitates nitrate of copper in shining blue-green, crystalline grains, but a concentrated solution produces a flocculent precipitate. (Braconnot.) — 2. On boiling carbonate of copper in the aqueous acid, the filtrate is found to contain in solution but a small quantity of salt, which crystallizes out on evaporation; if the residue on the filter be freed from the carbonate of copper still adhering to it, by means of dilute acetic acid, which dissolves but a small quantity of the maleate, the latter remains in the form of crystals, which may be washed with cold water. — 3. When a concentrated solution of acetate of copper is mixed with an equivalent quantity of maleic acid, and evaporated at a gentle heat, acetic acid goes off, and maleate of copper crystallizes out; the crystals must be washed with cold water.—The light blue crystals are but sparingly soluble in water even at a boiling heat, but dissolve readily in aqueous ammonia. (Büchner.)

Dried at 100°.			Büchner.
CuO	40	40·82	40·59
$C^4H^2O^4$	58	59·18	
$C^4HCuO^4 + Aq$	98	100·00	

Ammonio-maleate of Copper.—The dark blue solution of maleate of copper in ammonia may be evaporated, even near its boiling point, without loss of ammonia, and alcohol added to the concentrated solution precipitates the compound in the form of a neutral, azure-blue, crystalline powder, which gives off ammonia when heated with potash, and dissolves readily in water, but not in alcohol. (Büchner.)

Crystallized.			Büchner.
4 C	24	19·35	19·70
N	14	11·29	
6 H	6	4·84	4·98
CuO	40	32·26	31·96
5 O	40	32·26	
$NH^4O,C^4HCuO^4 + Aq$	124	100·00	

Mercurous Maleate. — The acid added to a solution of mercurous nitrate throws down white flakes. (Lassaigne, Braconnot.)

Maleate of Silver. — *a. Monomaleate.* The acid gives no precipitate with nitrate of silver, but maleate of potash or ammonia throws down a white precipitate. (Lassaigne, Braconnot.) — The white precipitate obtained with an alkaline maleate changes in a few hours to tolerably large, transparent and colourless crystals, having an adamantine lustre; after drying, it detonates slightly on the application of a gentle heat. (Liebig.) — The white precipitate obtained with equisetate of ammonia is curdy, like chloride of silver. After drying in the air, it is anhydrous, and does not lose weight at 120°. Between 148° and 150°, it decomposes with slight detonation, giving off carbonic acid gas, together with a sublimate of yellowish drops and small, strongly acid crystals which precipitate sugar-of-lead, and leaving carbide of silver in the form of a dark grey mass possessing the metallic lustre. (Regnault.)

Dried at 100°.			Regnault.
AgO	116	70·30	69·39
4 C	24	14·54	14·50
H	1	0·61	0·80
3 O	24	14·55	15·31
C^4HAgO^4	165	100·00	100·09

b. Bimaleate. Aqueous maleic acid, evaporated at a moderate heat with nitrate of silver yields white, shining needles. (Liebig, *Chim. org.* 2, 119.)

	Dried at 100°.		Büchner.
AgO	116	52·02	51·77
$C^8H^3O^7$	107	47·98	
$C^4HAgO^4,C^4H^2O^4$	223	100·00	

With the *Alkaloids* maleic acid forms salts which are readily soluble in water. (Pelouze.)

Maleic acid dissolves readily in strong *Alcohol* and in *Ether*. (Lassaigne, Pelouze, Regnault.)

B. Secondary Series.

Secondary Nucleus. C^4Cl^2.

Dichloride of Carbon.

Julin and Phillips & Faraday. *Phil. Trans.* 1821; also *Ann. Phil.* 17, 216; abstr. *Ann. Chim. Phys.* 18, 269.

Klumek.—Discovered by Julin in 1821; more exactly investigated by Phillips & Faraday.

Formation and Preparation. 1. Julin prepared nitric acid by distilling crude nitre with burnt green vitriol in cast iron retorts, connected with a Woulfe's apparatus; and whenever he used a particular kind of vitriol, which was obtained from the water of the Fahlun mine, and contained a small quantity of iron-pyrites, sulphur collected in the first connecting tube of the Woulfe's bottles, and in the second tube there were deposited a few grains of dichloride of carbon, mixed with sulphur, and with hydrochlorate and sulphate of ammonia; from these impurities they were freed by boiling with potash-ley, washing, drying, and sublimation. The cast-iron probably furnished the carbon, and the crude nitre the chlorine.

2. The compound likewise sublimes in fine silky needles when chloroform, C^2HCl^3, or protochloride of carbon, C^4Cl^4, is repeatedly passed through a strongly ignited porcelain tube filled with fragments of porcelain; if the heat be too strong, no chloride of carbon is obtained, nothing in fact but a deposit of charcoal. The needles are dissolved in ether, the filtrate evaporated to dryness, and the residue sublimed. (Regnault, *Ann. Chim. Phys.* 70, 104; also *Ann. Pharm.* 30, 350; also *J. pr. Chem.* 17, 229; *Ann. Chim. Phys.* 71, 381 and 386); *compare* VII, 348, 356.

Properties. White delicate needles (Julin), apparently four-sided (Phillips & Faraday); with a silky lustre (Regnault). The compound melts, boils, and sublimes between 175° and 200°, but may be sublimed without previous fusion at 120°, in which case the sublimate consists of long needles. (Julin.) Has a peculiar odour, something like that of spermaceti, but no taste. (Julin.) In the cold it is almost inodorous. (Regnault.)

				Phill. & Far.	Regnault.
4 C	24·0	25·32		24·15	
2 Cl	70·8	74·68		72·50	73·89
C^4Cl^2	94·8	100·00		96·65	

Decompositions. 1. Dichloride of carbon passed in the form of vapour through a red-hot porcelain tube filled with fragments of rock-crystal, is resolved into charcoal, which is deposited in the tube, and chlorine gas, which passes over. (Phillips & Faraday.) — 2. It burns in the flame of a candle with a greenish blue flame and a faint smell of chlorine, but goes out on being removed from the flame. (Julin.) The vapour mixed with oxygen over mercury takes fire on the passage of an electric spark, forming chloride of mercury and carbonic acid gas, the volume of which equals that of the oxygen consumed; if the quantity of oxygen be too small for complete combustion, expansion takes place in consequence of the formation of carbonic oxide. (Phillips & Faraday.) — 3. Three grains of the substance ignited with oxide of copper, yield chloride of copper, metallic copper, and 5·7 cubic inches of carbonic acid gas. (Phillips & Faraday.) — 4. The vapour of 1 pt. of chloride of carbon passed over lime heated in a glass tube brings it to a red heat, deposits charcoal, and forms a quantity of chloride of calcium which yields 2·95 pts. chloride of silver. (Phillips & Faraday.) [Carbonate of lime is also probably formed:

$$C^4Cl^2 + 3CaO = 2CaCl + CaO,CO^2 + 3C.]$$

5. Heated potassium burns in the vapour with a bright flame, forming chloride of potassium, and causing a deposition of charcoal. Phosphorus, iron, and tin, likewise separate charcoal from the vapour at a red heat, and take up the chlorine. (Julin.) — This compound is not decomposed or dissolved by nitric, sulphuric, or hydrochloric acid, or by boiling aqueous potash. It does not undergo any alteration in chlorine gas, not even when heated or exposed to sunshine. (Julin.) Its solution in alcohol or ether does not precipitate a solution of silver. (Phillips & Faraday.)

Combinations. Dichloride of carbon does not dissolve in water, either hot or cold. (Julin.) It dissolves readily in boiling *Alcohol* of sp. gr. 1·816, and separates out for the most part on cooling. — Soluble in *Ether.* (Phillips & Faraday.) — Dissolves in hot *Oil of Turpentine,* and separates out for the most part in needles on cooling. (Julin.)

ETHYLENE SERIES.

A. Primary Series.

Primary Nucleus. Ethylene. C^4H^4.

Respecting the manner in which the 4 At. carbon and the 4 At. hydrogen are probably united in ethylene, *vid.* VII, 32.

Deiman, Päts van Troostwyk, Bondt & Lauwerenburgh. *Crell, Ann.* 1795, 2, 195, 310, and 430; abstr. *Gilb.* 2, 201; abst. *Ann. Chim.* 21, 48.
Berthollet. *Mém. de l'Institut,* 4, 269; also *Scher. J.* 10, 575.
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Th. Saussure. *Ann. Chim.* 78, 57; also *Gilb.* 42, 349.
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Aetherin, Elayl, Ethene, Etherine, [*Vine*]; in the gaseous state: *Olefiant gas, Bicarburetted Hydrogen gas, Vinegas, Aethengas, ölbildendes Gas, ölerzeugendes Gas, Elaylgas; Gas oléfiant, Gas hydrogène deutocarboné.* — Discovered in 1795 by Deiman, Päts van Troostwyk, Bondt & Lauwerenburgh.

Formation. 1. When alcohol or ether is heated with oil of vitriol, &c., or alcohol with vitrefied boracic acid. (Ebelmen.) — 2. In the dry distillation of fixed organic bodies which contain but little oxygen, such as fats, resins, coal, &c.; also when the vapour of alcohol or ether is passed through a red-hot tube, filled with fragments of earthenware, a combustible gas is evolved, consisting for the most part of olefiant gas. The gas obtained by the dry distillation of caoutchouc is pure olefiant gas. (Himly.) Coal-gas produced by the distillation of coal contains at most from 10 to 20 per cent. of olefiant gas, but the portions which distil over last contain none (vid. *Coal*). The gas from alcohol or ether contains about one-half olefiant gas, if the vapour has been acted upon by red-hot earthenware, but none if the vapour has been passed through a red-hot *empty glass tube.* (Deiman, &c.)

Preparation. 1. *From Alcohol and Oil of Vitriol.* — *a.* By heating 1 pt. of alcohol of about 0·80 or 0·83 sp. gr. with 3 or 4 parts of oil of vitriol, in a flask connected with a gas-delivery tube. (Deiman, &c.) The mass swells up considerably, and is very apt to froth over. To prevent this, it is best to heat 16 pts. oil of vitriol, with only 1 pt. of alcohol, in the flask, till the mixture begins to blacken, and then pour in the rest of the alcohol by small portions at a time through an S-tube having a funnel and bulb. The evolution of gas then goes on regularly without any frothing. (Magnus, *Pogg.* 47, 524.)

Purification. The gas thus obtained is generally contaminated with alcohol-vapour, ether-vapour, sulphurous acid, carbonic oxide (J. Davy, Regnault, *Ann. Chim. Phys.* 69, 168, and others) and carbonic acid. The carbonic oxide amounts to at least 10 per cent.; olefiant gas obtained from alcohol and sulphuric acid is never purer than this. (J. Davy.) — The first third of the gas obtained from a given quantity of alcohol contains a little carbonic acid, but is perfectly free from carbonic oxide; the next third contains more carbonic acid, and about 4 per cent. of carbonic oxide; and the quantity of carbonic acid then increases so rapidly, that the last fifth of the evolved gas contains scarcely any ethylene, but consists almost wholly of carbonic oxide, carbonic acid, and sulphurous acid. (A. Vogel, Jun., *J. pr. Chem.* 25, 300.) — The ethylene gas may be contaminated from the beginning with a gas which appears to be marsh-gas, or a mixture of that compound with carbonic oxide; for on agitation with oil of turpentine, which absorbs 2½ times its volume of ethylene gas, there always remains a portion of gas unabsorbed. If 6 samples of the evolved gas, collected from the beginning to the end of the process at 6 equal intervals, be thus examined, the sulphurous and carbonic acids being removed by milk of lime, the residue unabsorbed by oil of turpentine amounts in the several portions to 10·5, — 10·0, — 10·1, — 13·1, — 28·3, — and 61·8 per cent. respectively. (Faraday.) — The alcohol and vapour may be removed by leaving the gas for several days over water, or better, according to Liebig (*Ann. Pharm.* 14, 150) by means of oil of vitriol; the sulphurous and carbonic acids, by strong potash or milk of lime. The gas is either shaken up with these liquids, or the liquids are placed in separate Woulfe's bottles or Liebig's bulb-apparatus, and the gas, as it is evolved, is made to pass slowly, first through oil of vitriol, then through potash-ley, and then again through oil of vitriol.—To obtain ethylene gas free from carbonic oxide, the first third of the evolved gas must, according to A. Vögel, be collected apart. But, according to Faraday, the gas thus collected would still contain about 10 per cent. of marsh-gas. Ethylene may however be obtained perfectly pure by saturating ether or alcohol with the gas, and then adding a quantity of water equal to 8 or 9 times the bulk of the liquid; about half of the absorbed gas is then evolved in small bubbles, the escape of which may be accelerated by heat. (Faraday.)

b. The vapour of 80 per cent. alcohol, boiling in a flask, is passed through a bent tube into a second flask, in which a mixture of 10 pts. oil of vitriol and 3 pts. water is constantly heated to its boiling point (between 160° and 165°), and the ethylene gas which is continuously evolved, together with vapour of water and smal lquantities of alcohol and ether-vapours, is collected by means of a gas-delivery tube adapted to this second flask. (Mitscherlich, *N. Ann. Chim. Phys.* 7, 12; also *Lehrb.* Aufl. 4, 1, 1, 195.)

2. *From Alcohol and Boracic acid.* 1 part of absolute alcohol is heated with 3 or 4 parts of finely pounded boracic acid in a flask which is provided with a very wide gas-delivery tube. A narrow tube would be stopped up by the hydrated boracic acid, which is very coherent, and consists of fibres standing upright. The ethylene gas thus obtained is contaminated with vapour of boracic ether, which, however, may be removed by agitation with water. (Ebelmen, *N. Ann. Chim. Phys.* 16, 136; also *J. pr. Chem.* 37, 353.)

3. *From Caoutchouc.* The elastic fluid evolved in the dry distillation of caoutchouc is passed through three cooled receivers, then through a bottle containing oil of vitriol, to remove a quantity of empyreumatic oil not previously condensed, after which the uncondensed gas is collected. This gas consists, first of carbonic acid, then of carbonic acid and carbonic oxide, and finally of pure ethylene. (Himly, *Dissert. de Cautschino.* Gott. 1835, 44.) [This gas might still contain vapour of caoutchene.]

Properties. 1. *In the Liquid state.* On compressing the gas by means of a pump into a condensing vessel cooled to about —110° by a mixture of ether and solid carbonic acid in vacuo, a transparent and colourless liquid is obtained, which does not solidify, even at —110°. (Faraday.)

The tensions, expressed in atmospheres, of two samples of this liquid are given under *a* and *b*; as, however, this liquid might also contain a certain quantity of the more volatile marsh-gas, in the condensed state, in which case the tension would be increased, the vessel was opened for a little while, in the case of another sample *c*, to allow this more volatile gas to escape, before the tension was observed. The residual liquid, however, always contains a little of the foreign gas: for if it be allowed to resume the gaseous state, and the gas treated with oil of turpentine, which absorbs the ethylene, a quantity of gas, amounting to 11 per cent., still remains unabsorbed; hence we must suppose that even the sample *c* possesses a greater tension than pure ethylene. (Faraday.)

Sample (*a*).		Sample (*b*).	Sample (*c*).		
	Atm.	Atm.		Atm.		Atm
−73·4	9·30	4·60	−76·1	4·60	−45·0	11·1
−67·8	10·26	5·68	−73·4	4·82	−42·8	12·2
−62·2	11·33	6·92	−70·6	5·11	−40·0	13·4
−56·7	12·52	8·32	−67·8	5·44	−37·2	14·7
−51·1	13·86	9·88	−65·0	5·84	−34·5	16·2
−45·6	15·36	11·72	−62·2	6·32	−31·7	17·7
−40·0	17·05	13·94	−59·4	6·89	−28·9	19·3
−34·5	18·93	16·56	−56·7	7·55	−26·1	21·1
−28·0	21·23	19·58	−53·9	8·30	−23·3	22·9
−23·3	23·89		−51·1	9·14	−19·3	24·8
−17·8	27·18		−48·3	10·07	−17·8	26·9
−12·2	34·70					
− 6·7	36·80					
− 1·1	42·50					

2. *In the Gaseous state.* Colourless. Sp. gr. 0·909 (Deiman, &c.) 0·967 (W. Henry); 0·9709 (Th. Thomson); 0·9784 (Saussure). Refracting power (I. 91). Has a suffocating and unpleasant odour, and causes death if inhaled in the pure state. Very inflammable; does not support the combustion of other bodies.

				Saussure.		Vol.	Density.
4 C	24	85·71	85	C-vapour	4	1·6640
4 H	4	14·29	15	H-gas	4	0·2772
C^4H^4	28	100·00	100	Ethylene or Olefiant gas	2	1·9412
					1	0·9706

Decompositions. 1. When electric sparks are passed for some time through olefiant gas, it is resolved into charcoal and hydrogen gas, the latter occupying twice the volume of the original gas. (Dalton, W. Henry.) 3 vol. olefiant gas, through which about 600 electric sparks have been passed, expand, without deposition of charcoal [?], to 5 vol. of a gas, from which chlorine no longer condenses an oil. (Deiman, &c.) — A red heat acts like electricity, excepting that it converts a portion of the gas into marsh-gas and an empyreumatic oil or stearoptene. If metals are present, they are often converted into carbides. Olefiant gas passed through a red-hot tube deposits charcoal, together with an empyreumatic oil, and yields a gas which is no longer condensed by chlorine. (Deiman, &c.) If the red-hot porcelain-tube through which the gas passes contains a spiral iron wire, empyreumatic oil and sooty carbon are obtained, while the iron becomes impregnated with carbon, and covered with graphite free from iron. (Sefström, *Pogg.* 16, 169.) — If the strongly ignited porcelain tube be filled with fragments of porcelain, the olefiant gas is converted, with deposition of carbon, into marsh-gas, with which a small portion of olefiant gas still remains mixed. The whole contains 1·63 pts. hydrogen to 6 carbon. (Marchand).—If the tube be filled with copper wire and heated to whiteness [in which case the copper must melt], a gas is obtained which burns with a dull blue flame, contains 1·92 pts. hydrogen to 6 pts. carbon, is but slightly condensed by chlorine in the dark, and is therefore nearly pure marsh-gas; but at a still stronger white heat, this gas likewise deposits its 2 At. carbon, and is converted into nearly pure hydrogen gas, containing 370 pts. hydrogen to 6 carbon. — Copper wire heated to low redness in olefiant gas, increases in weight by only 0·008 p. c., but becomes covered with a very thin blackish film, on the removal of which the metal appears red and is very brittle, capable of being rubbed to a fine powder, and exhibits a granular fracture. Finely divided copper obtained by the reduction of oxide of copper is converted under similar circumstances into brittle grains, and becomes covered with a black film of soot, containing from 4 to 12 per cent. of copper. (Marchand.) — Nickel wire thus treated becomes brittle, but apparently more susceptible of magnetism, and the finely divided metal becomes covered with a coating of soot, the uppermost layer of which contains from 2 to 4 per cent. of nickel. — Platinum wire likewise becomes covered with a black film of carbide of platinum, on the removal of which it appears corroded; if the heat be increased, the layer of carbide of platinum swells up to a loosely aggregated black mass, occupying 30 times the original bulk of the layer, and containing 11·5 p. c. platinum. (Marchand.) — When a mixture of 10 vol. olefiant gas, 20 vol. hydrogen, and 1 vol. oxygen is passed through a porcelain tube heated to dull redness, there is deposited on the colder part of the tube, but only at the beginning of the experiments, a small quantity of light, shining, fusible crystals, soluble in alcohol, and precipitated therefrom by water. (Bérard, *Ann. Chim. Phys.* 5, 297.) [Do these consist of naphthalin ?].

2. Olefiant gas mixed with air or oxygen gas may be set on fire by

flaming bodies, by the electric spark, and according to H. Davy, even by a red-hot coal or red-hot iron; but finely divided platinum does not generally set fire to the mixture, except at high temperatures. Liebig's *platinum-black*, at ordinary temperatures, causes slow combustion, resulting in the formation of carbonic acid; at 100° the combustion takes place more quickly. (W. C. Henry, *Pogg.* 39, 394.) — Platinum-black converts olefiant gas mixed with oxygen into acetic acid. (Döbereiner, *Ann. Pharm.* 14, 14.) — *Platinum*-paper-ash (II. 50), acts at 100° on a mixture of olefiant gas and oxygen, rising to a red heat, and sometimes producing inflammation. (Delarive & Marcet, *Ann. Chim. Phys.* 39, 328.) — *Spongy platinum* at 300° converts the mixture into carbonic acid and water. (Dulong & Thénard.) This slow combustion begins at 250°, and takes place completely, though slowly, at 271°. (W. Henry.) Even in presence of potash-ley, spongy platinum does not act at ordinary temperatures, or produces after a time mere traces of carbonic acid; but at 249°, it produces rapid, though tranquil combustion. (W. C. Henry.) — A *platinum-plate* prepared by the electric process (II. 47) does not act upon the mixture at ordinary temperatures, even in the course of several days (Faraday, *Pogg.* 33, 149); not even in presence of potash. (W. Ch. Henry.) — Neither *spongy iridium* nor *iridium-black* sets fire to the mixture at ordinary temperatures. (Döbereiner, *Schw.* 63, 465.)

In a mixture of 1 vol. olefiant gas and 1 vol. detonating gas (2 vol. H to 1 vol. O), a platinum-ball condenses nearly all the detonating gas, and forms but little carbonic acid; if the proportion of detonating gas be greater, more carbonic acid is formed. (W. Henry.) — If the olefiant gas be mixed with carbonic oxide and a quantity of oxygen sufficient to burn both the gases, spongy platinum at 177° produces slow combustion of the carbonic oxide only, the olefiant gas being left unaltered. (W. Henry.) — In a mixture of olefiant gas, marsh-gas, and oxygen, spongy platinum heated to 265° excites slow combustion of the olefiant gas only, not of the marsh-gas. (W. Henry.) — When a platinum-ball is introduced into a mixture of olefiant gas, marsh-gas, carbonic oxide, hydrogen and oxygen, the hydrogen and carbonic oxide burn first; then when the ball becomes hot, the olefiant gas; and, lastly, when the ball attains a red heat, the marsh-gas. (W. Henry, *Ann. Phil.* 25, 426.)

Olefiant gas burns in the air with a dense, white, highly luminous flame. (Deiman, &c.) — Mixed with at least 3 times its bulk of oxygen, and set on fire by the electric spark, it burns with a bright flash, and with a violence of explosion sufficient to burst very strong tubes. The tubes are much less likely to burst over mercury than over water; because the column of mercury below the gaseous mixture expands it to a greater degree before the explosion, than a column of water would. If a sufficient quantity of oxygen be present, 2 vol. olefiant gas consume 6 vol. oxygen, and form 4 vol. carbonic acid gas, besides water. (Saussure.) The 4 vol. C-vapour in 2 vol. olefiant gas form, with 4 vol. O-gas, 4 vol. CO^2-gas; the 4 vol. H-gas with 2 vol. O-gas form water. — A mixture of 2 vol. olefiant gas and only 2 vol. oxygen, set on fire by the electric spark, burns with a slight explosion, and yields nearly 8 vol. of a mixture consisting half of carbonic oxide and half of hydrogen; small quantities of carbonic acid and water are, however, formed at the same time. The 4 vol. C-vapour with 2 vol. O-gas form 4 vol. CO-gas; the 4 vol. H-gas are left unaltered. — 2 vol. olefiant gas exploded with 1·6 vol. oxygen, form 6·4 vol. of a gaseous mixture not absorbed by lime-water; sometimes when the gases are mixed in this and similar proportions, a small quan-

tity of charcoal is deposited; no carbonic acid is formed, or only a trace. A mixture of 2 vol. olefiant gas and 1 vol. oxygen is not inflamed by the electric spark. (J. Davy.) — A mixture of 2 vol. olefiant gas, 2 vol. hydrogen, and 1 vol. oxygen passed through a glass tube heated sufficiently to soften the glass, exhibits a slow combustion whereby only $\frac{1}{6}$ vol. oxygen gas is converted into carbonic acid; if the mixture contains carbonic oxide instead of hydrogen, explosion takes place. (W. Henry.)

3. A recently prepared mixture of 2 vol. olefiant gas and 4 vol. chlorine, set on fire by a flaming body, burns with a dark red flame, which passes right through the mixture, producing hydrochloric acid, and depositing carbon in the form of soot. (Deiman, &c.) — The 4 vol. H-gas combine with 4 vol. Cl-gas — the combination being attended with production of flame — and form 8 vol. hydrochloric acid gas, while the carbon is separated; to judge by the odour, a small portion of the carbon is at the same time converted into sesquichloride, C^4Cl^6. The mixture may likewise be set on fire by immersing in it a piece of Dutch metal, because that substance takes fire in chlorine gas. (Böttger.) — On one occasion, when olefiant gas [which, however, had not been purified and probably contained vapour of ether] was disposed in a layer above chlorine, inflammation took place spontaneously, attended with a bright flash, slight detonation, and deposition of a large quantity of charcoal. (Silliman, *Sill. Am. J.* 10, 365; also *Pogg.* 7, 534.) — 4. Sulphur heated in olefiant gas till it volatilizes, precipitates the carbon, and forms sulphuretted hydrogen (Deiman, &c.), the volume of which amounts to twice that of the decomposed olefiant gas. (H. Davy, J. Davy.) — If the sulphur is in excess, and the heat continued long enough, complete decomposition takes place — a small quantity of sulphide of carbon being likewise formed — so that, after the sulphuretted hydrogen has been absorbed by water, nothing remains but the carbonic oxide previously mixed with the olefiant gas.

5. When olefiant gas is heated in a retort with chlorate of potash, red oxide of mercury or protoxide of lead, there are formed — in the first case, with inflammation; in the second, scarcely and without inflammation — carbonic acid gas, occupying twice the volume of the decomposed olefiant gas, and water. (J. Davy.) — 6. A mixture of 2 vol. olefiant gas and 12 vol. nitric oxide does not explode on the passage of simple electric sparks, but is exploded by the discharge of a Leyden jar, and then yields 4 vol. carbonic acid and 6 vol. nitrogen, besides water. (W. Henry.) — 7. Olefiant gas is decomposed with evolution of light and heat, by hypochlorous acid gas, yielding water and chloride of carbon [probably C^4Cl^6I]; with the aqueous acid it slowly evolves chlorine and forms an oil, probably $C^4H^4Cl^2$. (Balard.) — 8. Olefiant gas passed, together with vapour of water, through a red-hot tube, yields water, sulphurous acid, sulphuretted hydrogen, carbonic acid, and charcoal. (Brault & Poggiale, *J. Pharm.* 21, 139.) — Anhydrous sulphuric acid absorbs the gas abundantly, with evolution of heat, forming water and sulphurous acid, and setting carbon free. (Aimé, *J. Pharm.* 21, 86.)

9. Olefiant gas passed through chlorochromic acid, $CrClO^2$, produces great heat, forms a large quantity of vapour of the oil of olefiant gas, C^4H^4,Cl^2, and renders the acid first opaque and pasty, then solid and pulverulent; if air be also present, the gas often takes fire, and the mass thus raised to a red heat gives off a dense vapour, and is converted into green oxide of chromium; if no inflammation takes place, there remains a dark brown, solid mass, probably $CrCl^2$. This mass deliquesces in the

air, forming a greenish brown liquid, from which ammonia throws down a greenish brown oxide, while chromate of ammonia remains in solution. (Wöhler, *Pogg.* 13, 298.) [The quantity of chlorine is not sufficient to convert all the chromium into $CrCl^2$; should not chromic oxide be formed at the same time?]— 10. *Chloride of iodine* absorbs olefiant gas, forming a colourless liquid which has an offensive smell and taste; solidifies at 0° forming crystalline laminæ, and is converted by the action of a larger quantity of olefiant gas, even at ordinary temperatures, into a solid crystalline mass. — With *Dichloride of sulphur* olefiant gas forms a stinking viscid liquid, less volatile than water and difficult to burn. (Despretz, *Ann. Chim. Phys.* 21,438.) Whether the formation of these compounds results from decomposition of the acting substances, is a point not yet determined.

Combinations. 1 vol. *Water* absorbs $\frac{1}{8}$ vol. olefiant gas, according to Dalton and Faraday; $\frac{10}{64}$ vol. according to Saussure.

Olefiant gas is capable of uniting with 2 At. *Chlorine, Bromine,* or *Iodine.*

It is absorbed by anhydrous *Sulphuric acid,* with great evolution of heat, forming either $C^4H^4,2SO^3$ (Regnault), or $C^4H^4,4SO^3$ (Magnus). — According to most authors, the gas is also abundantly absorbed by oil of vitriol. According to Liebig, on the contrary (*Ann. Pharm.* 9, 8), 1 vol. oil of vitriol absorbs only 1·4 vol. of pure olefiant gas. According to Brault & Poggiale (*J. Pharm.* 21, 138), the saturation of oil of vitriol surrounded by ice with the gas, produces a loosely united, greenish yellow compound, which gives off the absorbed gas on the addition of water or of aqueous alkalis. But, according to Hennel (*Pogg.* 14, 282) and others, the absorption is attended with formation of sulphovinic acid; and as this compound, when heated, gives off ether or alcohol according to the proportion of water with which it is mixed, a method is hereby afforded of converting ethylene into the other compounds of the ethylene-series. For the rest, vid. *Sulphovinic acid.*

At ordinary temperatures and pressures, 1 vol. alcohol or ether absorbs 2 vol.; 1 vol. oil of turpentine, $2\frac{1}{2}$ vol.; and 1 vol. olive oil, 1 vol. of olefiant gas. (Faraday.)

¶ Ethyl. $C^4H^5=C^4H^4,H$?

FRANKLAND.—On the isolation of Ethyl. *Inaugural Dissertation.* Marburg, 1849; *Ann. Pharm.* 71, 171; *Chem. Soc. Qu. J.* 2, 263; abstr. *Pharm. Centr.* 1850, 97; *N. J. Pharm.* 17, 146; *Jahresber.* 1849, 411. — Action of Light on Iodide of Ethyl. *Chem. Soc. Qu. J.* 3, 322; *Ann. Pharm.* 77, 221; abstr. *Pharm. Centr.* 1851, 369; *N. J. Pharm.* 19, 308; *Jahresber.* 1850, 460.

This radical has been obtained in the free state by the action of zinc on iodide of ethyl at high temperatures, and also by the action of light upon iodide of ethyl (VII, 171).

Preparation. Pure iodide of ethyl (for the preparation of which, vid. *Iodide of Ethyl*) is heated with finely divided zinc in a strong sealed glass tube immersed in an oil-bath. The granulated zinc is first introduced into the tube; the upper extremity of the tube drawn out, and bent twice at right angles; the liquid then introduced by heating and afterwards cooling the tube, while its open extremity dips into the liquid; the air exhausted by the air-pump; and lastly, the tube sealed and immersed in the oil-bath. The decomposition of the iodide of

ethyl begins at about 150°; white crystals are deposited on the zinc and on the glass, and there remains a colourless, mobile liquid, equal in bulk to about half the iodide of ethyl used. After about two hours' heating to 150°, the decomposition appears to be complete. — On breaking off the narrow end of the tube under water, a quantity of gas escaped, equal in volume to about 40 times the capacity of the tube, the mobile liquid at the same time gradually disappearing. This gas had an ethereal odour, burned with a bright flame, and was completely absorbed by recently boiled absolute alcohol. It was received over a dilute solution of sulphide of potassium, over which it was left to stand till all vapour of undecomposed iodide of ethyl was absorbed, the sulphide of potassium at the same time preventing the ingress of atmospheric oxygen by diffusion. The gas thus purified was found by careful eudiometic analysis to contain in 100 vol.: 50·03 vol. ethyl, C^4H^5; 25·79 hydride of ethyl, $C^4H^5.H$; 21·70 ethylene, C^4H^4; and 2·48 nitrogen. The calculated density of such a gaseous mixture is 1·504; Frankland found the sp. gr. by experiment to be 1·525.

The ethylene and hydride of ethyl are more volatile than the ethyl itself, and consequently escape in greatest abundance when the tube is first opened: and by collecting apart the gas which comes over after the evolution has become slow and regular, a gas is obtained, which when freed from ethylene and undecomposed iodide of ethyl by means of anhydrous sulphuric acid, and from sulphurous acid by potash, is found by analysis to be pure ethyl, C^4H^5.

Ethyl thus obtained is at ordinary temperatures a colourless gas, having a slightly ethereal odour (if perfectly pure, it would probably be inodorous); it burns with a white and very luminous flame. Its specific gravity was found by a diffusion-experiment, according to Graham's law, to be 2·0. It does not condense at −18° (0° Fah.) when passed, together with the hydride of ethyl, through a glass tube kept at that temperature; but in an Oerstedt's condensing apparatus, it condenses at + 3°, and under a pressure of 2¼ atmospheres, to a transparent, colourless, very mobile liquid; hence its boiling point under the ordinary pressure is probably about −23°.

Calculation.				Vol.	Density.		Vol.	Density.
4 C	24	82·77	C-vapour	4	1·6640	Or:	8	3·3280
5 H	29	17·23	H-gas	5	0·3465		10	0·6930
C^4H^5	53	100·00	Ethyl-gas	1	2·0105		2	4·0210
							1	2·0105

[For the discussion respecting the vapour-volume of ethyl and the other alcohol-radicals, *vid.* VII, 171–174.]

1 vol. ethyl-gas requires 6½ vol. oxygen to burn it completely, the 4 vol. C uniting with 4 vol. O to form 4 vol. CO^2, and the 5 vol. H with 2½ vol. O to form water. Mixed with half its volume of oxygen, and passed over spongy platinum, it remains unaltered at ordinary temperatures; but on the application of a gentle heat, the platinum becomes red-hot, a small quantity of charcoal is deposited, and water, together probably with marsh-gas, produced. It is not acted upon by nitric, chromic, or fuming sulphuric acid. With iodine and sulphur it does not combine even when heated; but at a red heat, sulphuretted hydrogen is formed, and charcoal separated. Chlorine does not act upon ethyl in the dark; but a dry mixture of the two gases in equal volumes, exposed to diffused light, undergoes a change of volume and forms a colourless liquid. Bromine acts upon

ethyl, when the two are gently heated together in the direct rays of the sun, but the products of the decomposition have not yet been examined.

Ethyl is insoluble in water, but soluble in absolute alcohol. 1 vol. absolute alcohol at 14·2°, and under a pressure of 744·8 mm. dissolves 18·13 vol. of the gas, but gives it up again on the addition of a small quantity of water.

Ethyl does not combine *directly* with any of the elementary bodies. According to the radical theory, however, it exists in a great number of compounds, which are analogous to the methyl-compounds enumerated at VII, 248.

Hydride of Ethyl or *Ethylide of Hydrogen.* C^4H^5,H.—1. Ethyl, under certain circumstances, is resolved into ethylene and hydride of ethyl. (Vid. p. 169; also VII, 171):

$$2C^4H^5 = C^4H^4 + C^4H^5,H.$$

2. This compound is also formed when iodide of ethyl is decomposed by zinc and other metals in presence of water or alcohol, or by sunshine in contact with water and mercury. (VII, 171; see also *Iodide of Ethyl.*)—3. When cyanide of ethyl (not quite anhydrous) is decomposed by potassium. (VII, 171.)

Preparation. When equal parts of water and iodide of ethyl are heated, in a sealed and exhausted glass tube, in the manner described on page 168, decomposition takes place at a lower temperature than when zinc is heated with iodide of ethyl alone; the decomposition is complete in about two hours. The liquid portion of the contents of the tube is thick, and solidifies on cooling to a white amorphous mass. On opening the tube under water containing sulphide of potassium, a large quantity of gas escapes, which by combustion with oxygen is found to have the composition of hydride of ethyl, C^4H^6.

This gas is colourless, nearly insoluble in water, but soluble in alcohol, which at 8·8°, and under a pressure of 665·5 mm. dissolves 1·22 of its own volume of it. It has at first a faint ethereal smell, but becomes quite inodorous after being treated with alcohol and fuming sulphuric acid. Does not liquefy at −18°, or even under a pressure of 20 atmospheres at + 3°. Chlorine does not act upon it in the dark; but on exposing the mixture to diffused daylight, the colour of the chlorine disappears altogether. 2 vol. chlorine with 1 vol. hydride of ethyl yield 2 vol. hydrochloric acid, together with an oily liquid having the same composition per cent. as Dutch liquid. (*Comp.* VII, 248; also *Chem. Soc. Qu. J.* 3, 338.)

					Vol.	Density.
4 C	24	44·44		C-vapour	4	1·6640
6 H	30	55·56		H-gas	6	0·4158
C^4H^5,H	54	100·00			2	2·0798
					1	1·0399

This gas was originally supposed by Frankland and Kolbe to be methyl; but the difference between the two is clearly shown by their behaviour with chlorine. (*Vid.* VII, 171, 248.) ¶

Ether. $C^4H^5O=C^4H^4,HO$.

SCHEELE. *Opusc.* 2, 132.
HERMBSTADT. *Chem. Vers. u. Beob.* 1, 45 and 116.
SCHRADER. *A. Tr.* 3, 2, 133.
LOWITZ. *Crell. Ann.* 1796, 1, 429.
V. ROSE. *Scher. J.* 4, 253.
LAUDET, DABIT, FOURCROY & VAUQUELIN, CADET, PROUST and FOURCROY. *Scher. J.* 6, 439.
TH. SAUSSURE. *J. Phys.* 64, 306; also *N. Gehl.* 4, 48; also *Gilb.* 29, 118.—Further: *Ann. Chim.* 89, 273; also *A. Tr.* 25, 2, 384.
P. F. G. BOULLAY. Phosphoric ether. *J. Phys.* 80, 199 and 208; also *Ann. Chim.* 62, 192; also *N. Gehl*, 4, 44; also *Gilb.* 44, 270.—Phosphoric ether. *Bull. Pharm.* 3, 149. — Arsenic ether. *Ann. Chim.* 78, 284; also *Schw.* 3, 394; also *Gilb.* 44, 270. — Sulphuric ether. *J. Pharm.* 1, 97.
DALTON. *Ann. Phil.* 15, 117; also *Schw.* 28, 363.
DESFOSSES. *Ann. Chim. Phys.* 16, 72; also *N. Tr.* 6, 1, 164.
J. DUMAS & POLYDOR BOULLAY. *J. Pharm.* 14, 1; also *Ann. Chim. Phys.* 36, 294; also *Pogg.* 12, 93.
LIEBIG. Constitution of Ether. *Pogg.* 31, 320; also *Ann. Pharm.* 9, 1. — *Ann. Pharm.* 30, 138.
MALAGUTI. Decomposition by Chlorine. *Ann. Chim. Phys.* 70, 338; also *Ann. Pharm.* 32, 15; also *J. pr. Chem.* 18, 29. — *N. Ann. Chim. Phys.* 16, 5; abstr. *Ann. Pharm.* 56, 286; abstr. *J. pr. Chem.* 32, 44.
REGNAULT. Decomposition by Chlorine. *Ann. Chim. Phys.* 71, 392; also *Ann. Pharm.* 32, 27; also *J. pr. Chem.* 19, 268.

Oxide of Ethyl, Ethylic oxide, Vinic Ether, Ethylic Ether, First Hydrate of Etherin, Aether; Vinäther, Aethyloxyd, erstes Aetherinhydrat; Oxyde d'Éthyle, Hydrate d'Éthérine [Lanavine]; and, according to the mode of preparation: *Sulphuric Ether, Schwefeläther, Schwefelnaphtha, Vitriol-naphtha, Aether sulphuricus, Naphtha Vitrioli, Ether sulfurique, — Phosphoric Ether, Phosphoräther, Ether phosphorique, — Arsenic Ether, Arsenikäther, Ether arsenique, — Fluoboric Ether, Fluoboronäther, Ether fluoborique, — Chlorzinkäther*, &c.

Val. Cordus, in 1540, first described the preparation of ether, which he called *Oleum Vitrioli dulce;* Frobenius, who first called it *Ether*, again directed attention to it in 1730; Val. Rose showed that the so-called sulphuric ether contains no sulphur. Fourcroy's suggestion that ether is alcohol deprived of a certain portion of oxygen and hydrogen, was confirmed by the analyses of Saussure, and of Dumas & Boullay. — Boullay discovered the preparation of ether by means of phosphoric and arsenic acids; Desfosses, that by fluoride of boron; Masson, that by chloride of zinc; Kuhlmann, that by bichloride of tin and other metallic chlorides.

Formation. — 1. By heating alcohol with substances endued with great affinity for water, such as sulphuric, phosphoric, and arsenic acid, fluoride

of boron, fluoride of silicium, or the chlorides of zinc, iron, tin, and antimony.

2. By the action of iodide of ethyl on potassium-alcohol: (Williamson, *Phil. Mag. J.* 37, 350; *Chem. Soc. Qu. J.* 4, 106; *comp.* V. 17, 201).

$$C^4H^5I + \begin{matrix} C^4H^5 \\ K \end{matrix}O^2 = 2C^4H^5O + KI.$$

Preparation. — 1. *By Sulphuric acid.* A mixture of alcohol having a sp. gr. of about 0·83, and oil of vitriol, in the proportion of 1 : 1 or 5 : 9 is distilled in a retort attached to a well cooled receiver, and fresh alcohol continually supplied by a tube passing through the tubulus of the retort and dipping into the mixture, so as to keep the liquid in the retort nearly at its original volume.

When equal parts of alcohol and oil of vitriol are used, a large portion of the alcohol passes over undecomposed; hence the proportion of 3 alcohol to 5 oil of vitriol, or of 2 : 3, or at most of 5 : 9 is preferable; if a still larger proportion of oil of vitriol were used, olefiant gas, &c., would be formed. — Formerly a mixture of equal parts of alcohol and oil of vitriol was distilled in a retort having 3 times the capacity of the mixture, till sulphurous acid began to be evolved; a second portion of alcohol, equal to $\frac{3}{4}$ of the first was then added, and the distillation continued till sulphurous acid gas again made its appearance; several smaller quantities of alcohol were then successively added to the residue, and the process repeated, till the residue lost its power of converting alcohol into ether. In this manner, Göttling (*Tascherb.* 1781, 182) obtained 6 pts. of ether from 1 pt. oil of vitriol. — It is better, however, to replace the decomposed alcohol continuously, as was first done by Boullay. (*J. Pharm.* 1, 107) and Geiger (*Repert.* 7, 122; 11, 58.) — In this manner 1 pt. oil of vitriol may produce 50 pts. of ether; but the ether which passes over towards the end of the distillation is contaminated with a considerable quantity of oil of wine. (Dominé, *N. J. Pharm.* 7, 159.) Ultimately also a large quantity of alcohol distils over undecomposed. — Boullay mixes 10 pts. of alcohol with 10 pts. oil of vitriol, and after 2 pts. have passed over, gradually drops, during the distillation, 10 pts. of alcohol, through a funnel inserted in the tubulus of the retort, and capable of being closed by a stop-cock, continuing the distillation till 15 parts have passed over; these yield 8 pts. of ether. Geiger mixes 2 pts. of alcohol with 3 pts. oil of vitriol, and inserts into the tubulus of the retort the longer and drawn out leg of a syphon, the other end of which dips into a vessel full of alcohol, so that during the ebullition, the alcohol runs continuously into the retort in a fine stream. By this method a small quantity of oil of vitriol may be made to convert a large quantity of alcohol into ether, equal in amount to half the alcohol used. If the alcohol be contained in a two-mouthed Woulfe's bottle, the supply of it may be stopped by closing the second aperture, and restored by blowing into the vessel. (Buchner, *Repert.* 21, 466.) — The tubulus of the retort may also be fitted with an S-tube, drawn out at the lower end, and having a funnel at the upper, the alcohol flowing into this funnel from a vessel provided with a stop-cock, which regulates the supply.

In the *Preparation on the Large Scale,* the mixture is heated either in a large tubulated glass retort, or in a large glass flask, or in a still of lead or cast-iron (which latter, however, as the iron dissolves in the sulphuric acid, continually weakens the acid and gives rise to evolution of hydrogen *gas, whereby* the perfect condensation of the ether-vapours is prevented).

Soltmann, according to the description given by Wittstock (*Pogg.* 20, 461), introduces a mixture of 14 lb. alcohol of sp. gr. 0·835 and 25 lb. common oil of vitriol into a tubulated glass retort, a foot in diameter, placed in a sand-bath; and, as soon as the mixture boils, allows fresh alcohol to run in through a glass tube with a knee-shaped bend, having a diameter of 3 or 4 lines, drawn out to the diameter of a line at the lower end, and dipping an inch below the surface of the mixture. The alcohol is contained in a bottle fitted at the lower part with a delivery-tube and a stopcock. The alcohol which runs out on opening the stopcock passes through a horizonal tube from 2 to 3 feet long into the knee-shaped tube, which is attached to the former by a caoutchouc joint, and thence flows into the mixture. The evolved ether-vapour passes from the neck of the retort into a Gedda's condenser, surrounded with cold water, and connected with a receiver. A strong fire must be made, and the operation regulated in such a manner that the supply of alcohol may equal the consumption, a point which may be ascertained by pasting a strip of paper on the outside of the retort, to mark the original position of the surface of the mixture. By this arrangement, 110 lbs. of alcohol may be run into the retort in the course of 16 or 20 hours. It is not advisable to continue the distillation longer, because the etherifying power of the mixture continually diminishes. To prevent the mixture from frothing over towards the end of the operation, a small quantity of water should be allowed to run in at that stage. — At the commencement of the distillation, two strata of liquid are obtained, viz., an upper ethereal and a lower watery stratum; but subsequently, when a larger quantity of undecomposed alcohol passes over, a uniform distillate is obtained. Oil of wine and sulphurous acid make their appearance in small quantity at the very beginning. (Wittstock.) — Boissenot (*J. Chim. méd.* 22, 538) gives the preference to this apparatus of Soltmann's, merely altering it by substituting for the retort a glass flask, having its cork bored with two holes, through which leaden tubes are inserted, the one serving to convey the alcohol into the flask, the other to carry off the vapours; he also condenses the vapours by means of a leaden cooling tube, instead of a Gedda's refrigerator. (*Comp.* also Stacker, *Repert.* 44, 292.)

The distillate thus obtained, the *crude ether*, consisting of ether, water, sulphurous acid, and sometimes also acetic acid, is agitated with aqueous solution of potash, or with milk of lime, till the layer of water and alcoholiferous ether, which floats on the lower layer consisting of water, alcohol, and sulphite of potash, no longer reddens litmus. This ethereal stratum is then separated by means of a siphon or a separating funnel, and once more distilled, till the greater part of the water, together with alcohol, remains behind. — It is better, after shaking up the crude ether with alkali and water, to distil the whole of it (not merely the upper layer), the ether then going over principally at the commencement of the distillation.

In Soltmann's method above described, the crude ether is agitated with an equal volume of water and some milk of lime, and the mixture distilled, without further separation, in a copper still. Ether of sp. gr. 0·725 then goes over first, amounting to $\frac{1}{3}$ of the crude ether, and free from oil of wine; — then a mixture of ether and alcohol in similar proportions to those which exist in the crude ether, — whence it may, like the latter, be treated with an equal quantity of water and rectified; — then alcohol containing oil of wine, amounting to between 20 and 25 per cent. of the

alcohol consumed; this part of the distillate is used, instead of fresh alcohol, as a supply in the next distillation (but not for mixing with oil of vitriol, because it then very soon deposits a large quantity of carbon;) — and, finally, water mixed with oil of wine passes over. — By this process 25 lb. oil of vitriol and 124 lb. alcohol yield 59 lb. of ether of sp. gr. from 0·720 to 0·725. As however part of the alcohol is recovered in its original state, we may reckon that in a manufacturing operation 100 pts. of alcohol yield 62·5 pts. of ether; the largest product that Wittstock was able to obtain amounted to 58 per cent. Alcohol obtained from potato-brandy, and containing fusel-oil, yields as good ether as purer alcohol. (Wittstock.)

The ordinary *Sulphuric Ether* thus obtained, whose specific gravity is about 0·78 or less, is converted into *Absolute Ether* by complete abstraction of the water and alcohol contained in it. — *a.* Lowitz first shakes it up with ignited potash, to separate the water, then, after decantation, with pulverized chloride of calcium, which unites with the alcohol, forming a heavy solution, and from this the pure ether may be poured off and distilled. — *b.* Saussure & Thénard agitate it with 1 or 2 pts. of water, to take up the alcohol; and after decanting the ether from the water, distil it over chloride of calcium, stopping the process however as soon as a third has passed over. — *c.* Gay-Lussac shakes it up with 2 pts. of water, leaves the decanted ether to stand for 12 days in contact with powdered quick-lime, agitating it frequently, and then subjects it to partial distillation, in the manner just described.

¶ Soubeiran (*N. J. Pharm.* 16, 321) describes an apparatus for the preparation of ether on the large scale, by which the ether is at once obtained in the rectified state, the first condensing vessels being kept (as in the more recently invented apparatus for the distillation of brandy) at a sufficiently high temperature to maintain the pure ether in the state of vapour. He recommends that the temperature of the etherifying mixture be kept constantly at 130°; because at 140° a gaseous hydrocarbon is constantly produced. — An apparatus for the rectification of ether has also been described by Hoyer. (*Arch. Pharm.* [2], 13, 140.) ¶

Absolute ether should form a clear mixture in all proportions with oil of copaiba; if it contains any water or alcohol, it forms an emulsion with considerable quantities of the oil. (Blanchet, *Ann. Pharm.* 7, 157.)

2. *By Phosphoric acid, according to Boullay.* By heating concentrated phosphoric acid with alcohol gradually passed into it. — Aqueous phosphoric acid of specific gravity 1·46 is heated to 112° in a tubulated retort, into the tubulus of which is inserted a funnel containing alcohol; this funnel is provided with two stopcocks, one above and the other below the alcohol, and its beak passes nearly to the bottom of the retort; by means of it a quantity of alcohol of 40° Bm., equal to that of the aqueous phosphoric acid, may be introduced into the acid by successive small portions. Each addition of the alcohol causes violent intumescence, and at first alcohol passes over, mixed with very little ether. But after $\frac{3}{4}$ of the whole quantity of alcohol has passed over, the remaining alcohol is more completely acted upon by the acid; the violent intumescence passes into a uniform and more general ebullition; and a larger quantity of ether is evolved. The receiver is then changed and the ethereal distillate, amounting to $\frac{3}{10}$ of the whole quantity of alcohol, collected. From this, by distillation over chloride of calcium, the ether may be obtained, in

quantity equal to $\frac{3}{10}$ of the whole amount of alcohol used. Up to this stage of the process, no gas is evolved and no charcoal separated. But if the heating be continued, the mixture blackens, still giving off a small quantity of ether, together with yellow oil of wine, water, and acetic acid. — If a more concentrated, syrupy phosphoric acid be used, the charring takes place sooner, and oil of wine passes over at an earlier stage of the process. (Boullay.)

3. *By Arsenic acid, according to Boullay.* In the same manner.—In the apparatus above described, 1 pt. of arsenic acid is heated with $\frac{1}{2}$ pt. water till it dissolves; the heat is then raised to the boiling point, and 1 pt. of alcohol gradually admitted as in the second method. Violent ebullition and spirting take place, and $\frac{4}{5}$ of the alcohol passes over unchanged; the liquid in the retort then becomes thinner, and boils more regularly, and on changing the receiver, yields an ethereal distillate, which is distilled once more alone, then twice over chloride of calcium, and yields ether amounting to between 10 and 12 per cent. of the alcohol used. Towards the end of distillation, the residue froths up, becomes brown or black, and is found to contain arsenious acid and carbon, besides vitreous arsenic acid; on the application of a still stronger heat, it gives off small quantities of carbonic and arsenious acid; but no oil of wine is formed. (Boullay.)

4. *By Fluoride of Boron, according to Desfosses.* (*Ann. Chim. Phys.* 16, 72.) Gaseous fluoride of boron evolved from a mixture of 2 pts. fluor spar, 1 pt. boracic acid, and 12 pts. oil of vitriol, is passed into 2 pts. of alcohol of 38° Bm.; the resulting fuming acid liquid distilled; the distillate neutralized with potash; the liquid again distilled, and the distillate rectified over chloride of calcium. The ether thus obtained agrees in all its properties with that which is prepared by means of sulphuric acid.

Properties. Transparent, colourless, very mobile. Refracts light strongly. Does not conduct electricity. Sp. gr. 0·758 (Lavoisier); 0·755 (V. Rose); — 0·732 (Lowitz); at 20° (when prepared as in 1, *a*); — 0·713 at 20° (1, *b*), according to Dumas & Boullay; — 0·7155 at 20° (1, *b*), according to Saussure & Thénard; — 0·7119 at 25° (1, *c*), according to Gay-Lussac; — 0·706 to 0·710 at 20° (Richter); — 0·690° (Boullay) prepared by (3); — 0·7358 (Pierre) — 0·73658 at 0° (Kopp). — Absolute ether does not solidify at —50° (Thénard), or even at —99°. (Mitchell, *Ann. Pharm.* 37, 356.) Ordinary ether, when agitated, deposits elongated shining laminæ, even at —31°, and solidifies entirely in a white crystalline mass at —44°. (Fourcroy & Vauquelin.) — Absolute ether boils under a pressure of 0·76 mm. at 35·66 (Gay-Lussac); at 35° to 36·6° (Dalton); at 34° under a pressure of 0·745 mm. (Dumas & Boullay); at 35·5 under a a pressure of 755·8 mm. (Pierre); at 34·9 under a pressure of 752 mm. (Andrews); at 35·6°. (Person.) When exposed to the air it evaporates, producing a considerable degree of cold. — Vapour-density 2·25 (Dalton); 2·586 (Gay-Lussac); 2·581 (Despretz.) — Tension of the vapour: According to Ure (*vid.* I, 262, 263); according to Dalton, 7·5 inches of mercury at 2·2°; 15 inches at 17·8°; 30 inches at 35·5°; 60 inches at 55·5°; 126 inches at 78·3°; and 240 inches at 104·4. Refracting power of the vapour. (I, 95.) — Ether has a penetrating ethereal odour, which affects the head; its taste is strong, sweetish, and cooling.

			Dumas & Boullay.	Saussure.	Ure.	Dalton.
4 C	24	64·87	65·05	67·98	59·6	51·9
5 H	5	13·51	13·85	14·40	13·3	14·4
O	8	21·62	21·24	17·62	27·1	33·7
C^4H^5O	37	100·00	100·14	100·00	100·0	100·0

	Vol.	Density.	Or:	Vol.	Density.
C-vapour	4	1·6640	Ethylene-gas	2	1·9412
H-gas	5	0·3465	Vapour of water	1	0·6239
O-gas	½	0·5546			
Ether-vapour	1	2·5651	Ether-vapour	1	2·5651

Gay-Lussac showed (*Ann. Chim. Phys.* 14, 316) that ether may be regarded as a compound of olefiant gas and water.

According to the nucleus-theory, ether may be regarded either as C^4H^4,HO, or as C^4H^5O,H^2. (VII, 33.) The latter formula is regarded by Malaguti (*N. Ann. Chim. Phys.* 16, 28) as the more probable, on account of the behaviour of ether in certain reactions. — Laurent & Gerhardt, however, double its atomic weight, so as to make its vapour not monatomic, but diatomic, like most organic gases; according to this view, ether may be regarded as a copulated compound of 1 At. alcohol with 1 At. ethylene. — Dumas & Boullay regard ether as the first hydrate of ethylene or olefiant gas, which, according to them, has very strong basic properties: $=C^4H^4,Aq$. This formula is consistent with the nucleus-theory; only that theory does not suppose that the O and H contained in ether are actually united in the form of water. — Robiquet (*J. Pharm.* 20, 489) objects on good grounds to the supposed basic nature of ethylene; and the same reasons tend to disprove the supposed basic nature of ether.

According to the *Ethyl-theory* first propounded by Berzelius (*Ann. Pharm.* 6, 173) and, as it appears, at the same time by J. Kane (*Dublin, J. of Med.* and *Surg. Sc.* 2, 348), and further developed by Liebig (*Ann. Pharm.* 9, 1; 19, 270; 23, 12), *Ether* $=C^4H^5,O$, *i.e.* it is the oxide of a metalloïdal radical, *Ethyl* $= C^4H^5$, which was hypothetical when the theory was first propounded, but has since been isolated; (*vid.* p. 168.) Ethyl corresponds to ammonium, NH^4, and oxide of ethyl to oxide of ammonium, NH^4,O. The oxide of ethyl has, like the oxide of ammonium, a basic character, and forms corresponding salts, which in fact are those compound ethers designated in this Handbook as vinic ethers of the third class. (*Vinester.*) Thus, *nitrate of ammonium-oxide* $= NH^4,O + NO^5$, and *nitrate of ethyl-oxide* (*nitric ether*) $=C^4H^5,O + NO^5$. When 2 At. of certain acids unite with 1 At. ethyl-oxide, a copulated acid is formed, which may be regarded as a compound of a salt of ethyl-oxide with a hydrated acid. Thus, *sulphovinic acid* $= HO,SO^3 + C^4H^5O,SO^3$; and *sulphovinate of baryta* is a double salt, composed of sulphate of ethyl-oxide and sulphate of barium-oxide, $=BaO,SO^3 + C^4H^5O,SO^3$. — If ether were a hydrate, it ought to be decomposed by the voltaic current (for the same reason it cannot be an oxide: *A. Connell*), and its water would be replaceable by a metallic oxide; and if ethylene were a strong base, its two hydrates, ether and alcohol, might be expected to exert an alkaline reaction. According to the ethyl-theory, also, ether [and alcohol] should exhibit an alkaline reaction, and should combine at once with acetic acid, for example, to form acetic ether; and ethereal compounds of that nature should be decomposed by alkalis and metallic salts in the same manner as other saline

compounds. But ether is a base of a different kind from potash, its compound with sulphuric acid, viz. sulphovinic acid, not precipitating baryta-salts. (Liebig. *Ann. Pharm.* 19, 270.) These observations amount to an admission of many of the difficulties to which the ethyl-theory leads. (Comp. VII, 216, 217.) — Regnault (*Ann. Chim. Phys.* 71, 415; also *J. pr. Chem.* 19, 284) pronounces against the ethyl-theory. — Mitscherlich (*N. Ann. Chim. Phys.* 7, 12) supposes that, since ether does not act as a base, ethers of the third class must contain, not ether, but a basic compound isomeric therewith, which may be distinguished by the term *oxide of ethyl.* — Liebig subsequently proposed (*Ann. Pharm.* 30, 138) to deduce the compounds of the vinic series, not from ethyl, C^4H^5, but from another hypothetical radical, *Acetyl*$=Ac=C^4H^3$. According to this hypothesis, olefiant gas would be Ac,H; ether$=AcH^2O$; alcohol$=AcH^2O+HO$; hydrochloric ether$=AcH^2Cl$, &c. — ¶ Williamson, Gerhardt, and Chancel, regard ether as water in which 2 At. H are replaced by ethyl, viz. as $\left.\begin{matrix}C^2H^5\\C^2H^5\end{matrix}\right\}O$, according to Gerhardt's atomic weights (VII 27), or $\left.\begin{matrix}C^4H^5\\C^4H^5\end{matrix}\right\}O^2$, according to the atomic weights adopted in this Handbook. (*Vid.* VII, 17.) ¶

Decompositions. 1. Ether-vapour passed through a *red-hot tube* is for the most part resolved into a gaseous mixture, apparently containing olefiant gas, marsh-gas, and hydrogen, and into aldehyde, water, and small quantities of charcoal, empyreumatic oil, and naphthalin. Ether passes unchanged through a tube filled with pumice-stone, and heated to 300°; but if the tube contains spongy platinum, decomposition takes place even at 220°: an effect of contact, therefore. (Reiset & Millon, *N. Ann. Chim. Phys.* 8, 290.)—When the vapour is passed through a red-hot empty *glass tube,* neither charcoal nor empyreumatic oil is obtained; the resulting gaseous mixture has a density of 0·709, and burns with a light reddish flame. Mixed with chlorine, it condenses by only $\frac{1}{7}$ vol. without yielding any oil of olefiant gas, and the $\frac{6}{7}$ vol. residue burns with a bluish flame of a totally different character. The entire gas mixed with chlorine, and set on fire, deposits a large quantity of soot. — When ether-vapour is passed through the red-hot tube of a tobacco-pipe, or through a glass tube filled with fragments of a clay-pipe, or with alumina or silica (lime and magnesia do not exert this action), the resulting gaseous mixture contains a large quantity of olefiant gas, and therefore when mixed with chlorine, diminishes to one-half, with formation of oil; the residue likewise burns with a bluish flame. (Deiman, &c.) — 100 pts. of ether, of sp. gr. 0·7155, passed through a red-hot porcelain tube, deposit therein 0·255 pts. charcoal and 0·85 pt. of a mixture of naphthalin, a brown liquid empyreumatic oil soluble in alcohol, and a brown tarry empyreumatic oil insoluble in alcohol but soluble in ether; it also yields a combustible gaseous mixture, *oxidized carburetted hydrogen* (VII, 251), mixed only at the beginning of the decomposition, and only to the extent of 1 per cent. with carbonic acid, and having in the dry state a sp. gr. of 0·6605 at the beginning, and 0·6250 towards the end. (Saussure.) — Absolute ether passed through a wide red-hot glass tube filled with fragments of glass, deposits a trace of charcoal, and is resolved into aldehyde, water, and a combustible gaseous mixture, which burns with a bright flame, contains 17·6 pts. (5 At.) hydrogen to 82·3 pts. (4 At.) carbon, and is a mixture of olefiant gas and marsh-gas; the decomposition is represented by the following equation:

$$6C^4H^5O = 2C^4H^4O^2 + 2HO + 3C^4H^4 + 2C^2H^4.$$

(Liebig, *Ann. Pharm.* 14, 134, and 137.) [Can water remain in contact with olefiant gas and marsh-gas at a red heat, without forming carbonic oxide?]

Absolute ether, either cold or boiling, is not decomposed by an electric current from 216 pairs of 4-inch plates, but stops it completely. Even if it contains in solution hydrate of potash, dry chromic acid, corrosive sublimate, or bichloride of platinum, it still remains unacted upon by a battery of 50 two-inch plates. If it be impregnated with hydrochloric acid gas, it gives off hydrogen gas at the negative pole, and acquires a yellow colour from separation of chlorine. (Arthur Connell, *Edinb. Transact.* 13, 331; also *J. pr. Chem.* 5, 183; abstr. *Pogg.* 36, 492.)

2. Ether is easily set on fire, and *burns* with a white, moderately luminous flame, which smokes only when the supply of air is limited. Its vapour mixed in equivalent proportion with air or oxygen gas explodes on the passage of an electric spark or by contact with a flaming body. If ether be allowed to evaporate in 100 vol. oxygen, till the gas is expanded to only 103 and 110 vol., an electric spark passed through the detonating tube containing the mixture produces complete combustion, accompanied by strong detonation, 100 vol. ether-vapour consuming about 600 vol. oxygen gas, and producing 400 vol. carbonic acid. (Dalton.) 1 vol. ether-vapour contains 4 vol. C-vapour, 5 vol. H-gas, and $\frac{1}{2}$ vol. O-gas; 4 vol. C-vapour with 4 vol. O-gas form 4 vol. CO^2-gas, and 5 vol. H with $\frac{1}{2}$ vol. O-gas already contained in the ether, and 2 vol. O-gas more form water. — When ether evaporates in the air in large rooms, the mixture explodes on the introduction of a burning body, with the force of a powder-magazine. About 18 pounds of ether, accidentally evaporated in Pagenstecher's cellar, produced an explosion which alarmed the whole city of Bern; shook all the houses; killed two men and threw their bodies to a considerable distance, blew off the roof of the cellar; and laid in ruins the shop situated above it. (*Repert.* 28, 409.)—If however the air or oxygen be mixed with too large a quantity of ether-vapour, the mixture will not take fire, because the excess of ether-vapour exerts too much cooling action. (Saussure, II, 33, 4.) — When 100 vol. oxygen, by taking up ether-vapour, are expanded to 200 vol. (which may be effected by the introduction of ether in considerable quantity), the electric spark produces but very imperfect combustion or none at all; but if the 100 vol. are expanded to only 150 vol., violent detonation takes place, and there remain 300 vol. of a mixture of carbonic acid with a large quantity of hydrogen, marsh-gas, and carbonic oxide. 100 vol. air, to produce an inflammable mixture with ether-vapour, must not be expanded to more than 105 vol. (Dalton.) Hence no explosion takes place in the air-passages, on setting fire to the air expired by animals which have been rendered insensible by ether-vapour—the small quantity of oxygen contained in the expired air being mixed with too much nitrogen, carbonic acid, vapour of water, and ether-vapour, to form an explosive mixture.

3. *Slow Combustion.* Ether-vapour mixed with air, and in contact with platinum and certain other metals or other solid bodies, which in some cases may be cold, in others must be heated but not to redness, burns slowly, forming water, carbonic acid, *Lampic* or *Etheric acid*, and an aqueous mixture of aldehyde, acetal, acetic acid, formic acid, and a peculiar substance, which chiefly imparts to the vapour its pungent odour and tear-exciting action, and appears to take part in the reducing action which the entire mixture exerts on heavy metallic oxides.

When ether is dropped upon Liebig's platinum-black (VI, 278, *c*, *γ*) triturated to a fine powder with water and then well dried, and the moistened part is covered with dry platinum-black, a violent emission of sparks takes place, followed by inflammation. (Liebig.)

In other cases the platinum, if previously heated, rises to a red-heat when introduced into the mixture of air and ether-vapour, but does not usually set fire to it. Thus with the following arrangements:

When a drop of ether is left to evaporate in a cold glass vessel containing air, and a hot spirally wound platinum wire introduced into the vapour, the metal becomes red-hot; in the dark, a pale phosphorescent light is observed above the wire, especially when it ceases to glow. A pungent acid substance is produced at the same time. Similar effects are produced with palladium wire and fine palladium foil. (H. Davy, *Gilb.* 56, 246.) A thin piece of platinum foil attached to a glass handle (II, 26, 6) and immersed while hot in a beaker-glass, the bottom of which is covered with ether, is brought into a state of continuous glow, and gives off a suffocating vapour. — Moderately heated spongy platinum becomes red-hot in air mixed with ether-vapour. (Dana, *Sill. Amer. J.* 8, 198; also *Schw.* 13, 380.)

In the *Lamp without Flame*, or *Glow-lamp* (II, 26, 5), a spiral wire of platinum, or certain other metals, acts in the manner just described; with silver-wire, however, the action does not take place so readily.

Böttger's Glow-lamp. — A spirit-lamp is provided with a wick of asbestus, the fibres of which at the upper end are spread out as much as possible; the wick is then saturated with a paste of platinum-salammoniac and alcohol, and thoroughly ignited before the blowpipe. When this lamp is filled with ether, and the wick set on fire and blown out again, the spongy platinum in the wick is kept, by the imperfect combustion of the ether vapour, in a state of continuous glow, which is not so easily put out by the draught of air as that of the ordinary glow-lamp. At the same time there rises a pungent, strongly tear-exciting vapour, proceeding from the so-called *lampic* acid. To condense this vapour, the upper part of the apparatus is surrounded with a helm, the bottom of which surrounds the wick at some little distance, so as to admit access of air. (Böttger, *J. pr. Chem.* 10, 61.)

Faraday passes air mixed with ether-vapour through a heated glass tube containing platinum wire or platinum foil, into a well cooled receiver.—A. Connell inverts a funnel—whose beak is fitted with a helm, and within which is suspended a ball of platinum wire—over a dish filled with ether, and placed in a larger dish, but in such a manner that a current of air may enter between the outer dish and the bottom of the funnel. The lampic acid then condenses, partly in the helm, partly in the funnel, in quantity amounting to about $\frac{1}{16}$ of that of the ether.

Lampic acid may also be formed by the imperfect combustion of ether mixed with air, in presence of non-metallic solid bodies.

If a flame be held under a basin filled with ether, but at such a distance as not to set fire to the vapour, the odour of lampic acid becomes perceptible. (Geiger.) Hence also in the distillation of ethereal vegetable extracts, if an increase of heat is required towards the end of the operation to expel the remainder of the ether, and the receiver does not fit close, so that the air has access to the extract, the same odour is perceived. (Geiger & Hesse, *Ann. Pharm.* 5, 67.) The action is probably assisted by the heated upper parts of the sides of the vessel.—When ether is dropped into a retort heated in the sand-bath to 100° or upwards, or into

a platinum capsule exposed to the vapour of boiling water, Leidenfrost's phenomenon is produced (I, 277, 278), accompanied by a pale blue flame visible only in the dark, and not capable of setting fire to other bodies (on the approach of a burning body it changes to the common ether flame), and the tear-exciting vapour of lampic acid is evolved. (Döbereiner, *J. pr. Chem.* 1, 75.) The same phenomenon has been more recently observed by Boutigny (*J. Chim. méd.* 13, 589), who heated the metal or porcelain dish to 260°. If therefore a tubulated retort having the lower part of its bulb removed, be held over a heated metal or porcelain dish, and ether be dropped at intervals through the tubulus on to the dish, the lampic acid will condense in the neck of the retort, and may be collected; if, however, the dish be too strongly heated, rapid combustion takes place. (R. F. Marchand, *J. pr. Chem.* 19, 57.) — In a very shallow dish placed in a hot sand-bath, a mixture of ether with an equal quantity of water and a small quantity of nitric acid (but not hydrochloric) or ether placed in a layer above oil of vitriol, evolves first ether-vapour, then vapour of aldehyde, having a very powerful odour. (Simon, *Pogg.* 41, 658.)

Hot gum-charcoal held over ether continues to glow, and acts like platinum. (Murray.) A similar effect is likewise produced by gum-tragacanth, myrrh, wood, indigo, and bones, and the quantity of acetic acid produced by the combusion is greater, as the ignition of the charcoal is feebler. (H. B. Miller, *Ann. Phil.* 28, 17; also *Br. Arch.* 23, 222.)

The glowing extremity of a glass rod or a piece of porcelain, held over ether, exhibits a small blue flame, and forms a large quantity of acid. Red-hot lime produces a like effect, and at the same time gives out a white phosphoric light. (Miller.)

The so-called *Lampic* or *Etheric acid*, first observed by H. Davy, and examined by Faraday (*Quart. J. of Sc.* 3, 77; also *Ann. Chim. Phys.* 4, 359; also *Schw.* 20, 183), is a transparent and colourless liquid of sp. gr. 1·015 (up to 1·027, Böttger), sour and harsh taste, and disagreeable pungent odour; its vapour excites a copious flow of tears. When decomposed by nitric acid, it yields oxalic acid, and when heated with manganese, it gives off carbonic acid with strong effervescence. (Daniell.) It is turned brown by oil of vitriol, giving off at the same time a vapour which strongly attacks the eyes and smells of formic acid. (Böttger.) It also turns brown when boiled. (Martens & Stas.) It dissolves oxide of copper, forming a liquid from which copper is thrown down in the form of a red powder on boiling. With mercuric oxide it forms a white crystalline powder, consisting of mercurous acetate. (Daniell.) It dissolves mercuric oxide with effervescence when heated, and deposits, on cooling, mercurous formiate, together with a small quantity of mercurous acetate. (Connell.) With oxide of silver it forms a solution which silvers the containing vessel on being heated. (Böttger, *J. pr. Chem.* 10, 62.) With the aid of heat, it separates the metal from an aqueous solution of mercurous nitrate, nitrate of silver, or chloride of gold, and also, on addition of soda, from bichloride of platinum, the metal being often deposited as a coating on the surface of the vessel. (Daniell.) When boiled with corrosive sublimate, it precipitates calomel, together with a trace of metallic mercury. (Böttger, *J. pr. Chem.* 12, 335.)

When lampic acid has been distilled till $\frac{1}{3}$ has passed over, the distillate is neutral and destitute of reducing action [the aldehyde had probably escaped in consequence of imperfect condensation]; it does not smell of *ether, but gives* out the pungent odour of lampic acid, and burns with a

blue flame; the residue in the retort has retained its reducing power, and in contact with mercuric oxide; and with the aqueous solution of mercuric nitrate, which solidifies at the same time, it instantly forms mercurous acetate. By neutralizing it with alkalis and evaporating, salts are obtained closely resembling the acetates in composition, but often of a brown colour, and less disposed to crystallize. Their solution still possesses the reducing power; so likewise does the acid, *e.g.* that which is separated from the baryta-salt by sulphuric acid. (Daniell, *Gilb.* 61, 350. — *Ann. Phil.* 19, 469; Daniell & Phillips, *Gilb.* 75, 101.)

Daniell & Phillips regard lampic acid as aqueous acetic acid mixed with a resinous substance, to which the reducing action is due. Liebig (*Ann. Pharm.* 14, 160) ascribes this action to the presence of aldehyde, $C^4H^4O^2$, and to that of an acid called *Aldehydic acid*, $C^4H^4O^3$ (not yet obtained in the free state, and of doubtful existence); the aldehyde is likewise the cause of the browning which takes place on mixing the acid with oil of vitriol, and on evaporating it in contact with alkalis, which produce aldehyde-resin. — A. Connell (*N. Ed. Phil. J.* 14, 237; *Phil. Mag. J.* 11, 512; also *J. pr. Chem.* 12, 321; *Phil. Mag.* 29, 353) showed that lampic acid contains besides acetic acid, a quantity about 5 times as great of formic acid. Moreover, he supposes that lampic acid contains an ethereal or empyreumatic or resinous substance, and more recently he has stated that aldehyde is to be found in it, but not aldehydic acid. According, therefore, to the quantity of oxygen which unites with the ether, there is formed sometimes aldehyde, sometimes acetic acid, sometimes formic acid. Lampic acid saturated with oxide of lead yields on evaporation, first crystals of formiate of lead, then of acetate. Those noble metals which are reduced by formic acid are also reduced by lampic acid, and in both cases with effervescence.

Martens & Stas (*J. pr. Chem.* 18, 375; also *N. Br. Arch.* 20, 181) consider lampic acid as an aqueous mixture of formic acid, acetic acid, aldehyde, and a peculiarly strong-smelling substance, which they are inclined to regard as aldehydic acid. When lampic acid is agitated with ether, the upper ethereal film decanted, rectified over magnesia, saturated with ammonical gas, and then exposed to a temperature of $-90°$, crystals of aldehyde-ammonia are obtained. The lower watery film, neutralized with oxide of lead, and mixed with an equal quantity of alcohol, yields a white powder of formiate of lead, which crystallizes in needles from a solution in hot water; the remaining liquid, when evaporated, yields by evaporation needles of acetate of lead, and a mother-liquor which gives no more crystals, but a peculiar-smelling, amorphous mass of acetate of lead, with which a peculiar reducing substance is mixed. This substance turns brown at 65°, and yields an acid substance having a suffocating odour; its aqueous solution mixed with nitrate of silver, reduces the silver with effervescence; when the solution is precipitated by sulphate of copper, and the filtrate left to evaporate, crystals of acetate of copper are first obtained, then paler crystals having the odour of the amorphous mass, and a mother-liquor which deposits metallic copper at 100°, whilst acetate of copper remains in the solution.

All the products hitherto found in the so-called lampic acid are insufficient to account for its peculiarly pungent odour and its tear-exciting action. These actions were formerly ascribed to an empyreumatic oil produced at the same time. But, according to Schönbein, (*Ueber die langsame und schnelle Verbrennung der Körper*, Basel, 1845, S. 1 and 39), these actions are due to the presence of a compound of ozone with ethylene

formed at the same time. When a few drops of ether are left to evaporate in a bottle containing air, and a hot platinum wire wound round with a spiral at the lower end is introduced into the bottle, the wire exhibits in the dark a bluish phosphoric appearance, and in daylight produces a dingy black-blue vapour, which quickly diffuses itself and disappears. The air in the vessel, which, for shortness, may be called *Ozonized Ethylene-air*, acquires the pungent odour and tear-exciting action of lampic acid; it likewise shows all the oxidizing actions of ordinary ozonized air (produced by the slow combustion of phosphorus) viz. blueing of starch-paper moistened with iodide of potassium, browning of paper wetted with solution of hydriodic acid, browning of aqueous iodide of potassium, decolorization of iodine-solution, oxidation of ferrous salts, conversion of ferrocyanide of potassium into ferricyanide, decolorization of indigo-solution, blueing of paper moistened with tincture of guiacum, conversion of sulphurous into sulphuric acid, decomposition of sulphuretted hydrogen dissolved in water, decolorization of paper browned with sugar-of-lead solution and sulphuretted hydrogen, &c.; but platinum-foil immersed in ordinary ozonized air is negative to another piece of platinum in the hydro-electric circuit, whereas that which has been immersed in ozonized ethylene-air remains unaltered. Frequent inspiration of ozonized ethylene-air produces a sensation of tightness in the throat, accompanied by catarrhal symptoms.

Water agitated with ozonized ethylene-air takes up the ozonized ethylene very quickly, the remaining air being thereby almost wholly deprived of its pungent odour and of the power of producing the oxidizing actions above mentioned, whereas common ozonized air is but little altered in these respects by agitation with water. The solution thus obtained, *Ozonized Ethylene-water*, possesses the odour and other reactions of ozonized ethylene-air; but they continually diminish when the ozonized ethylene-water is kept for some time in stoppered bottles, and are immediately diminished in a sensible degree by boiling. When the water is distilled, both the distillate and the residue still exhibit oxidizing properties; but the distillate in a lower degree. Iron filings or mercury agitated with the ozonized ethylene-water deprive it of its peculiar properties, and dissolve in it; the mercury-solution is precipitated by hydrochloric acid, and deposits metallic mercury when boiled; it therefore contains mercurous oxide, and probably also formic or acetylous acid. When considerable quantities of ozonized ethylene-air are made to act upon iodide of potassium, or when a small quantity of iodide of potassium is dissolved in ozonized ethylene-water, and the brownish liquid is distilled, iodine passes over first, then Faraday's iodide of carbon, $C^4H^4I^2$, in shining scales having an aromatic odour; they are insoluble in water, but soluble in alcohol and ether, to which they impart a sweet taste; they melt easily, and then give off iodine. On the other hand, aqueous iodide of potassium does not form $C^4H^4I^2$ with ether and chlorine-water.

Ozonized ethylene-air may also be formed by passing the proper quantity of olefiant gas into ozonized air prepared in the ordinary way; the ozonized air loses thereby the power of rendering an immersed platinum plate more negatively electrical, and instead of the odour of ozone and olefiant gas, acquires the pungent odour of lampic acid; generally, indeed, this mixture exhibits all the reactions of the ozonized ethylene-air above described, and likewise easily gives up its active principle to water, so that the water acquires all the properties of ozonized ethylene-water; when pretty well saturated, it has a biting taste, and likewise yields $C^4H^4I^2$ by distillation with iodide of potassium. If ozone be regarded as

a compound isomeric with peroxide of hydrogen = HO^2, the pungent, tear-exciting principle of lampic acid and ozonized ethylene-air is perhaps $C^4H^4,2HO^2$. Slowly burning ether (like slowly burning phosphorus) induces the water in the air to form ozone by taking up 1 At. O. The ozone, however, does not in this case remain free, but unites with the C^4H^4 of the ether to form this pungent substance. The production of aldehyde and acetic acid is perhaps connected with this formation of ozonized ethylene. (Schönbein.)

Even at ordinary temperatures, ether kept for some time in a bottle containing air produces acetic acid and other products. — Absolute ether set aside for two years in a vessel standing in the light, and frequently opened, acquires the power of reddening litmus, and leaves, when distilled, an acid residue which boils at 53°, mixes with water, forms an acetate with potash, and when mixed with oil of vitriol, yields a precipitate consisting of an oil having a burning taste. (Planché, Gay-Lussac, *Ann. Chim. Phys.* 2, 98, and 213; also *N. Tr.* 1, 2, 249.) — Boullay found acetic acid produced in bottles containing only small quantities of ether. — According to N. E. Henry (*J. Pharm.* 13, 119), ether turns acid even in perfect darkness, especially in contact with water, probably because it generally contains a little acetic ether, which, by contact with water, is resolved into alcohol and acetic acid. According to this view, the acetic acid is not a product of the slow combustion of ether, but a decomposition-product of acetic ether.

4. When *Chlorine gas* is made to act upon ether, and no means employed to check the rise of temperature which accompanies the action, the ether takes fire and charcoal is separated. — When a quantity of ether between ½ dram and 1 dram is placed at the bottom of a bottle of the capacity of 2 litres, filled with chlorine, and having its mouth loosely covered with paper, white fumes are given off after a few hours, and subsequently explosion takes place, accompanied by flame and considerable deposition of charcoal. (Cruickshank, *Nicholson, J.* 5, 20.) When chlorine gas is passed through ether, every bubble sets fire to the ether, which becomes heated throughout, and ultimately there remains a black tarry mass. At −10° inflammation does not take place so readily, and not all, even on the application of heat, if a sufficient quantity of chlorine has been previously passed through at −10°. (Liebig, *Ann. Pharm.* 1, 220; also *Pogg.* 24, 283.) — When a piece of gypsum is soaked in ether, the ether set on fire in the air, and then plunged into chlorine gas, it continues burning for a short time with a slightly smoky flame.

If the inflammation of the absolute ether through which the chlorine is passed be prevented by surrounding it with a freezing mixture till it has lost the capability of taking fire under the influence of chlorine, and the passage of the chlorine be continued as long as hydrochloric acid continues to form, — while the temperature is gradually raised to 135°...142°, by application of heat from without, — 2 At. hydrogen in the ether are ultimately replaced by 2 At. chlorine, and the ether is converted into bichlorinated ether, $C^4H^8Cl^2O$:

$$C^4H^{10}O + 4Cl = C^4H^8Cl^2O + 2HCl.$$

In this reaction, the chlorine is at first quickly absorbed, the liquid acquiring a yellow colour, and increasing in bulk; afterwards the absorption becomes slower, and a violent evolution of hydrochloric acid gas takes place; this however gradually diminishes. At first only 1 At. hydrogen

appears to be replaced by chlorine, and monochlorinated ether, C^4H^4ClO, formed:

$$C^4H^5O + 2Cl = C^4H^4ClO + HCl.$$

The hydrochloric acid hereby produced converts a small portion of the ether into water and chloride of ethyl:

$$C^4H^5O + HCl = C^4H^5Cl + HO.$$

This water decomposes part of the monochlorinated ether — which is not immediately converted into bichlorinated ether — yielding aldehyde and hydrochloric acid:

$$C^4H^4ClO + HO = C^4H^4O^2 + HCl.$$

And, lastly, the aldehyde is converted, by the further action of the chlorine into chloral, $C^4HCl^3O^2$.

$$C^4H^4O^2 + 6Cl = C^4HCl^3O^2 + 3HCl.$$

Hence, at the commencement, during the violent evolution of hydrochloric acid gas, a small quantity of chloride of ethyl passes over, and the bichlorinated ether obtained at the end of the process is mixed with a certain quantity of chloral. (Malaguti, *Ann. Chim. Phys.* 70, 338.)

The following observations were made previously to those of Malaguti. — When chlorine is passed through ether, 8 pts. of the ether (which in the further progress of the experiment is not heated from without) increase by 3 pts.; and on addition of a small quantity of water, the yellowish mixture is resolved into an upper watery stratum of aqueous hydrochloric acid and a lower oily stratum of heavy hydrochloric ether. (Berthollet, *Ann. Chim. Phys.* 1, 426.) — Dry chlorine gas passed to saturation through ether at 0°, is half converted into hydrochloric acid which escapes; and there remains a liquid, of sp. gr. 1·23, which resembles the oil of olefiant gas, $C^4H^4Cl^2$, excepting that it has a more penetrating odour and a sharper taste. (Morin, *Ann. Chim. Phys.* 43, 239; also *Pogg.* 19, 61.) If the liquid be gradually heated to the boiling point, and the passage of the chlorine continued as long as hydrochloric acid continues to form, an oil is obtained, which smells like sesquichloride of carbon, has a density of 1·611, and boils at 139°. When the oil is heated with oil of vitriol, a small portion of it blackens and gives off hydrochloric acid, but the greater part goes over unaltered. It does not diminish when shaken up with water or with aqueous potash; but when mixed with alcoholic potash, it deposits chloride of potassium, and on subsequently mixing the liquid with water, an aromatic oil is precipitated. (Liebig, *Ann. Pharm.* 1, 220.) [Probably, therefore, bichlorinated ether in a less pure state than as it was subsequently obtained by Malaguti.] — There is always formed a tolerably large quantity of chloral; for in the formation of chloride of ethyl, water is produced, and further quantities of chlorine act upon this water + ether, in the same manner as upon alcohol, forming first aldehyde and then chloral. (Regnault, *Ann. Chim. Phys.* 71, 421.)

If the passage of the chlorine be still longer continued, and the liquid exposed to sunshine, the ether is finally converted partly into perchlorinated ether, C^4Cl^5O, partly into sesquichloride of carbon, C^4Cl^6, and chloraldehyde, $C^4Cl^4O^2$. (Regnault, *Ann. Chim. Phys.* 71, 392; Malaguti, *N. Ann. Chim. Phys.* 16, 5):

$$C^4H^5O + 10Cl = C^4Cl^5O + 5HCl;$$

and

$$2C^4H^5O + 20Cl = C^4Cl^6 + C^4Cl^4O^2 + 10HCl.$$

Under the influence of a winter sun, the principal product is perchlorinated ether, but in summer, sesquichloride of carbon and chloraldehyde are chiefly produced. But the sun of June, 1845, produced scarcely anything but perchlorinated ether. This variation in the effects appears to be due, not to any difference of care in drying the chlorine, but to causes which are as yet unknown. If the product consists mainly of chloride of carbon and chloraldehyde, it gives off the chloraldehyde when distilled at a gentle heat, in the form of a fuming liquid having a suffocating odour. (Malaguti.) — Laurent (*Ann. Chim. Phys.* 66, 317) states, that on exposing the mixture to sunshine, he obtained crystals of oxalic acid, together with an oil. — When ether is shaken up with chlorine-water in which hydrate of chlorine is suspended, it first absorbs the chlorine, then gives up hydrochloric acid to the water, and afterwards contains chloride of carbon in solution. (Serullas, *Ann. Chim. Phys.* 45, 190; also *J. Chim. méd.* 7, 1.)

5. *Bromine* appears to act like chlorine. — The hyacinth-red solution of bromine in ether loses its colour in a few days, and yields hydrobromic acid. (Balard.) — Ether perfectly saturated with bromine appears, after 12 days standing, to be completely converted into hydrobromic acid, bromide of ethyl, bromal, a large quantity of heavy hydrobromic ether, and probably also formic acid. If the mixture be distilled, the receiver being changed when half has passed over, and the third fourth collected alone, this latter portion is found to consist of *heavy hydrobromic ether*, which may be purified by agitation with potash-ley and rectification over burnt lime. This heavy hydrobromic ether is a transparent, colourless, strongly refracting liquid, heavier than oil of vitriol, volatile, of penetrating agreeable odour, and permanently sweet taste. It contains 8·63 per cent. C, 1·36 H, 80·94 Br, and 9·07 O, and therefore consists of $C^4H^4Br^3O^3$. Its vapour passed over red-hot lime, is resolved into bromide of calcium mixed with charcoal, and a gas which burns with a bright flame. [According to the reaction here described, 3 Br must evolve 3O from 3CaO; and these 3O with the 3O of the compound are sufficient to convert all the 4C into 4CO, and the 2H into 2HO; hence nothing can be given off but a mixture of carbonic oxide and hydrogen, which burns with a pale blue flame, and no charcoal can remain with the bromide of calcium.] — On boiling it with potash-ley, bromoform passes over, while formiate of potash and bromide of potassium remain behind. [This reaction cannot be expressed stoïchiometrically.] — When it is boiled with oil of vitriol, bromine is set free, and another colourless liquid passes over. (Löwig, *Pogg.* 36, 551.) — When a solution of bromine in ether is placed for a few days in contact with water, the water takes up hydrobromic acid; the ether becomes gradually decolorized, and if then carefully evaporated, gives off a small quantity of water, emits an odour like that of camphor or turpentine, reddens litmus strongly (even after previous washing with water), and finally leaves an oil floating on the water, probably a peculiar bromide of carbon. (Serullas.) — When bromine standing under water at 0° is saturated with chlorine gas, and an equal volume of ether added to the resulting *chloride of bromine*, the water immediately takes up hydrochoric acid; and on frequently renewing the water and agitating, the chlorine gradually dissolves in the water as hydrochloric acid, and afterwards also part of the bromine as hydrobromic acid. Hence if the washing be stopped as soon as the wash-water becomes coloured yellow by chlorine (and therefore contains no hydrobromic acid), the whole of the bromine remains dissolved

in the remaining ether in the form of bromide of carbon, but the ether does not contain a trace of chlorine; hence this process affords a means of separating chlorine from bromine. The ethereal liquid thus obtained behaves just like that which is prepared with bromine alone. (Serullas, *Ann. Chim. Phys.* 45, 190.) — Ether shaken up with aqueous *Protochloride of Iodine* withdraws this compound from the water, but in the course of a few hours gives up the chlorine to the water in the form of hydrochloric acid, whilst all the iodine remains in the ether. (Serullas.) — Ether likewise withdraws *Terchloride of Iodine* from its aqueous solution; but decomposition soon takes place, especially on evaporation; if the evaporation be rapid, there remains a brown solution of protochloride of iodine; if it be slow, crystals of iodine separate out, whilst the chlorine acts chiefly on the ether. (Soubeiran, *J. Pharm.* 23, 53.)

6. *Phosphorus* converts ether, even when the air is completely excluded, into several acids containing phosphorus. — Pure ether set aside for a few days in a bottle filled with it, and containing finely-divided phosphorus, turns sour, and yields, if it be decanted and distilled to $\frac{1}{20}$ in a stream of carbonic acid gas, a very acid, thin syrup, which, when neutralized with baryta, yields three kinds of salts; the first is insoluble in water, the second sparingly, the third readily soluble. The last, the *phosphatate of baryta*, is yellowish white; indistinctly crystalline; leaves, when ignited, a residue containing charcoal; is turned brown by oil of vitriol; and in the state of aqueous solution, gives no precipitate with chloride of calcium, but precipitates corrosive sublimate, nitrate of lead, and nitrate of silver. The lead-precipitate is shrunken and yellowish. (Zeise, *Ann. Pharm.* 41, 33; also *J. pr. Chem.* 26, 84.)

7. Concentrated *Chloric* or *Bromic acid*, agitated with ether, acts violently upon it, giving off chlorine or bromine vapour, and forming acetic acid. (Serullas, *Ann. Chim. Phys.* 45, 203.) Chloric acid dropped upon ether sets it on fire. (Langlois, *J. Chim. méd.* 16, 382.)

8. *Nitric acid* does not act on absolute ether at ordinary temperatures, but very energetically when heated, the products being nitric oxide, hyponitric acid, carbonic acid, acetic acid, and oxalic acid. (Boullay.)— When oil of vitriol is added to a tranquil mixture of ether and fuming nitric acid prepared in the cold, violent inflammation takes place. (Brugnatelli, *Scher. J.* 4, 251.) — Ether mixed with a solution of sulphate of nitric oxide in oil of vitriol (II, 450, β), becomes heated, froths up strongly, turns violet, and is converted into a brownish, viscid mass. (Döbereiner, *Schw.* 8, 253.) — The solution of uranic nitrate in ether, when exposed to sunshine, deposits uranous oxide, and acquires the odour of nitrous ether. (Bucholz.)

9. Ether cooled below 0° takes up anhydrous *Sulphuric acid*, and forms a yellow oil, from which ether, when shaken up with it, extracts sulphovinate of oil of wine, whilst the lower acid stratum contains *Isethionic acid*, together with hydrated sulphuric acid. (Magnus, *Pogg.* 27, 378; *comp.* Liebig, *Ann. Pharm.* 13, 35; Regnault, *Ann. Pharm.* 27, 12.) — Oil of vitriol does not act upon ether at ordinary temperatures; but at higher temperatures, either sulphovinic, or althionic, or isethionic acid, makes its appearance in the mixture; and on the application of a still stronger heat, sulphurous acid, olefiant gas, and sulphovinate of oil of wine, are given off, while a carbonaceous mass remains, probably similar to that which is obtained with alcohol. As sulphovinic acid, under certain cir-

cumstances, yields alcohol, this reaction affords a means of reconverting ether into alcohol. (Hennel, *Pogg.* 14, 281.) — A mixture of equal parts of oil of vitriol and ether blackens at 69°, at which temperature it boils, gives off olefiant gas, carbonic acid gas, water, [sulphovinate of] oil of wine, and acetic acid, leaving a residue which is resinous at first, but afterwards coaly. (Boullay, *J. Phys.* 80, 203.) — 3 pts. of oil of vitriol and 1 pt. of ether distilled together yield, from the beginning, oil of wine together with a small quantity of ether; with the proportion of 2 : 1, one-third of the ether passes over unaltered at first, and afterwards oil of wine, mixed with a small quantity of ether. — 4 pts. oil of vitriol, 1 pt. ether, and 1 pt. water, yield [sulphovinate of] oil of wine, the first portions of which, containing a little ether, float upon water, whilst the latter portions sink to the bottom. Water and sulphurous acid are likewise evolved, and the residue thickens, chars, and swells up. — With 2 pts. oil of vitriol, 1 pt. ether, and from ½ to 1 pt. water, half the ether passes over unaltered, and afterwards oil of wine follows. (Deslauriers, *J. Pharm.* 2, 481.) — Oil of vitriol at ordinary temperatures absorbs the vapour of ether, which may then be separated from it unaltered by adding water carefully, so that no rise of temperature shall take place; if the mixture becomes heated, sulphovinic acid is produced. (Magnus, *Pogg.* 27, 386; also *Ann. Pharm.* 6, 171.) A mixture of equal parts of oil of vitriol and ether [the mixing having been probably attended with some evolution of heat] resolves itself, when left at rest, into ether, which floats at the top, and contains but a trace of sulphovinic acid, and a lower stratum of oil of vitriol mixed with sulphovinic acid [and probably also with ether]. When the whole mixture is distilled, the sulphurous acid and olefiant gas which pass off towards the end of the operation, are accompanied by sulphovinate of oil of wine. (Serullas, *Ann. Chim. Phys.* 39, 152; also *Schw.* 55, 171.) — The acid which forms in the residue on heating oil of vitriol with ether, up to the point when olefiant gas begins to escape, is not sulphovinic but althionic acid. (Regnault, *Ann. Pharm.* 25, 43.) — A mixture of equal parts of ether and oil of vitriol, heated to 100°, yields, when saturated with baryta, ordinary sulphovinate of baryta. (Gerhardt, *Chim. org.* 1, 146.) — A mixture of oil of vitriol and ether heated to 170°, leaves a residue containing isethionic acid. (Marchand, *J. pr. Chem.* 15, 16.)

10. Ether saturated with *Hydrochloric acid gas* yields, by distillation, a liquid resembling chloride of ethyl, C^4H^5Cl. (Süersen, *A. Gehl.* 5, 69.)— Ether saturated with *Hydriodic acid gas* is immediately resolved into an upper layer of a pale yellow and a lower layer of a dark red colour, which appears to contain hydriodous acid. (A Connell, *Phil. Mag. J.* 18, 356.)

11. Ether decomposes many of the heavy metallic *Chlorides*, especially under the influence of light, abstracting the chlorine wholly or partially, and thereby undergoing decompositions which require more exact investigation than they have hitherto received. — The brownish ethereal solution of chloride of uranous oxide deposits all the uranium, when exposed to light, in the form of a green protochloride of uranium. (Gehlen.) — The yellowish brown solution of *Sesquichloride of Iron* in ether is decolorized by exposure to sunshine for a few days, hydrochloric acid being formed, and the whole of the iron separated in the form of protochloride, none of which remains in solution. — In sunshine the decomposition takes place behind colourless and blue glass, but not behind red glass. (A. Vögel, *J. Pharm.* 1, 197.) — The solution of 1 pt. sesquichloride of iron in ether of sp. gr. 0·73 (therefore nearly anhydrous), placed in a bottle completely filled with

it, and exposed to sunshine, deposits drops which unite at the bottom, and soon solidify in the form of crystalline hydrated protochloride of iron, ultimately mixed with a carbonaceous substance, a number of lighter greyish green flocks, and small quantities of an oil insoluble in water and acids, but slightly soluble in ether. The supernatant ether, after sufficient exposure to the sun, becomes brown-black; fumes, in consequence of containing a large amount of free hydrochloric acid; appears to be free from iron; and is resolved by distillation into a black-brown resin containing a trace of ferrous chloride, insoluble in water, soluble in acids and in alcohol, dissolving with yellow colour in boiling potash-ley, whilst a more highly carbonized substance remains in solution, — and a distillate consisting of hydrochloric acid and ether, which, after being treated with potash, exhibits the pure odour of ether, and consequently contains no chloride of ethyl. (Fr. Jahn, *Ann. Pharm.* 19, 321.) — Kerner (*Ann. Pharm.* 29, 68) also obtained, with 1 pt. sesquichloride of iron and 4 pts. ether, crystals of ferrous hydrochlorate; and on distilling the supernatant ether, a black-brown resin was obtained, having a peculiar odour, easily soluble in ether, but insoluble in water, alcohol, or oil of turpentine, and a distillate rich in hydrochloric acid. — The solution of sesquichloride of iron in hydrated ether, exposed in winter to sunshine and to diffused daylight, assumes at first a grass-green colour, depositing green crystals of hydrated ferrous chloride, but finally becomes quite colourless, and gives up all its iron, the last portions of which are deposited in colourless crystals, the liquid then separating into two strata. The lower stratum, which has not yet been thoroughly examined, contains chlorine; the upper is a mixture of ether, aldehyde, chloride of ethyl, and free hydrochloric acid. (Jonas, *N. Br. Arch.* 37, 36.) — Similar phenomena are exhibited by the ethereal solution of sesquichloride of iron, when alcohol is added to it, as in the *Tinctura tonico-nervina Bestuscheffii*, excepting that part of the resulting protochloride of iron is held in solution by the alcohol. — A solution of 1 pt. sesquichloride of iron in 4 pts. ether and 2 pts. alcohol, which has a density of 0·85, deposits on exposure to light, drops of a light green liquid, which solidifies in crystals amounting in quantity to half the sesquichloride of iron used; and the supernatant, colourless liquid, which still contains iron, and has a density of only 0·806, yields, when distilled, a mixture of ether and a large quantity of free hydrochloric acid, and apparently also of chloride of ethyl, whilst a resin remains, though in smaller quantity than when alcohol is not used. (Kerner.) — If the air has access to the decolorized liquid, it resumes its yellow colour.—*Comp.* Landerer (*Repert.* 53, 80.)

The yellow-green ethereal solution of *Protochloride of Copper* loses its colour when exposed to light, in consequence of the formation of dichloride of copper, which is precipitated on the addition of water. (Gehlen.)—This reduction likewise takes place in a bottle made of blue glass, but not in one of red glass; the decolorized liquid forms a colourless mixture with ammonia. (A. Vogel.) — The ethereal solution of *corrosive sublimate* exposed to light under blue, but not under red glass, deposits white shining, crystalline scales, containing calomel and mercurous carbonate. (A. Vogel, *J. Pharm.* 1, 196.) — The ethereal solution of *Terchloride of Gold* exposed to light deposits the gold often in the crystalline state. (Sage, *Scher. J.* 3, 106.) — The ethereal solution of *Bichloride of Platinum* (*q. v.*) is also decolorized by light, but without separation of metal.

12. *Terfluoride of chromium* dissolves in ether, forming a yellow

liquid, which soon exhales the odour of chloride of ethyl, and deposits a dark green film of acid hydrofluate of chromic oxide, so that the supernatant liquid no longer contains fluorine. (Unverdorben.)

13. Many *heavy metallic oxides* decompose ether by giving up oxygen to it. — Ether placed in contact with ferric oxide gradually turns sour. (N. E. Henry.) — The solution of osmic acid in ether deposits all the osmium in the metallic state in the course of 24 hours. (Berzelius.) — A mixture of 2 pts. ether, 2 pts. peroxide of manganese, and 1 pt. oil of vitriol, gently heated, rises spontaneously to the boiling point, whereupon the greater part of the ether passes off undecomposed, and a portion is converted into carbonic and acetic acid. (Scheele.) — 37 pts. (1 At.) ether distilled with 264 pts. (6 At.) manganese, and 294 pts. (6 At.) oil of vitriol, yield a liquid containing sulphuric acid and smelling of oil of wine, but no formic acid. (Döbereiner, *Ann. Pharm.* 14, 188.) — When ether is distilled with chromic acid and oil of vitriol, acetic acid passes over. (Dumas & Stas, *Ann. Chim. Phys.* 73, 155.)

14. Ether-vapour passed through a heated mixture of lime and hydrate of potash yields a mixture of hydrogen and marsh-gas; the residue contains carbonate of potash, but no acetate or formiate. Perhaps the acetate of potash formed at the commencement was immediately resolved into carbonic acid and marsh-gas (Dumas & Stas, *Ann. Chim. Phys.* 73, 155; also *Ann. Pharm.* 35, 164; also *J. pr. Chem.* 21, 376.) — When caustic potash is boiled in a retort and ether is poured into it by means of a funnel-tube drawn out at the end and passed into the tubulus, a carbonaceous substance is deposited and ether having a very unpleasant odour passes over. (Boullay.) — When ether is left for 4 years in contact with potash, lime, magnesia, ferrous oxide, iron, lead, or zinc, a small quantity of acetate is formed, proceeding, however, not from the decomposition of the ether, but from that of the acetate of ethyl generally mixed with it. Under these circumstances, potash and lime impart an offensive odour to the ether. (N. E. Henry, *J. Pharm.* 13, 119.)

15. *Potassium* and *Sodium* immersed in ether of the highest degree of purity oxidize but very slowly, giving off hydrogen gas. (Gay-Lussac & Thénard, *Recherches*, 1, 382.) — As soon as the potassium becomes covered with a crust of potash, all further action is stopped. (Liebig, *Pogg.* 31, 335.) — The continued action of potassium or sodium produces crystalline compounds of ether with the anhydrous alkalis, which, when exposed to the air, are converted into alkaline acetates. If the metals act for a considerable time in excess, the ether is completely decomposed, with formation of a yellow opaque jelly. (Kuhlmann, *Ann. Pharm.* 33, 103.)

Combinations. — When *Water* is agitated with ether, two layers are formed, the upper consisting of ether containing a little water, and the lower of water which has dissolved $\frac{1}{10}$ of ether (or $\frac{1}{14}$, according to Boullay); this lower liquid has a density of 0·96, and boils for a short time at 39·4°, till the small quantity of ether contained in it is expelled. (Dalton.)

Ether mixes in all proportions with liquid *Carbonic acid.* (Thilorier.) When carbonic acid is condensed in a tube containing ether, striæ are formed in the liquid, which soon becomes milky. On opening the tube, the carbonic acid escapes with violent effervescence, and leaves more or less unaltered ether behind. (Mitchell, *Ann. Pharm.* 37, 358.) — Under the ordinary pressure, ether absorbs 2·17 vol. carbonic acid gas. (Saussure.)

Absolute ether dissolves $\frac{1}{20}$ of its weight of *Phosphorus* when that substance is agitated with it in the finely-divided state at 20°. The solution smells of phosphorus; takes fire when dropped upon boiling water; produces phosphoric acid after some time, especially under the influence of light or heat; deposits phosphorus in the pulverulent state on the addition of alcohol, and a further quantity on the subsequent addition of water, whereas water alone does not throw down any thing. Ordinary ether dissolves only $\frac{1}{220}$ pt. phosphorus. (Brugnatelli, *Ann. Chim.* 24, 73; Bucholz, *Theorie u. Praxis*, Aufl. 2, 2, 293.) — 1 vol. ether absorbs 2 vol. *Phosphuretted Hydrogen gas.* (Graham.)

1 pt. *Sulphur* dissolves quickly in 12·5 pts. ether at ordinary temperatures. The colourless solution smells of sulphuretted hydrogen, deposits the sulphur when evaporated, blackens lead-salts, dissolves to a somewhat less amount in water than pure ether, and without precipitation of sulphur. (Favre, *A. Gehl.* 4, 227.) — Ether absorbs *sulphurous acid gas.* — *Oil of vitriol* mixes with an equal or a smaller quantity of ether, producing rise of temperature; if this latter effect be prevented, a colourless mixture is obtained which becomes rose-coloured when warmed, and decomposes on the application of a stronger heat. (pp. 186, 187). If to this mixture of the two liquids in equal parts, there be gradually added a larger quantity of ether, and rise of temperature be prevented, 2 pts. or even more of ether may be made to unite with 1 pt. of oil of vitriol; but a small quantity of oil of vitriol shaken up with a large quantity of ether, does not mix with it, but takes up only a small quantity of the ether. (Boullay.) — A mixture of 100 pts. oil of vitriol and 3 pts. ether boils at 142°, giving off the ether. (Mitscherlich, *Lehrb.* Aufl. 4, 1, 246.) — Oil of vitriol rapidly absorbs ether-vapour; if the vapour be enclosed in the Torricellian vacuum, it disappears instantly on the introduction of oil of vitriol. (Liebig, *Ann. Pharm.* 14, 148). — If 18 vol. ether be poured on the top of 1 vol. oil of vitriol, the volume of the latter becomes doubled by absorption of water from the ether [also by absorption of ether]; after the lapse of 24 hours, the upper ethereal stratum is found to contain sulphuric acid. Ether, shaken up with dilute sulphuric acid, takes up scarcely a trace of it; if left in contact with the acid for some time, it takes up a larger quantity, but the resulting mixture becomes turbid on the addition of pure ether. (Simon, *Pogg.* 41, 657). — Ether, shaken up with dilute sulphuric acid, does not take up any acid from it; but, when agitated with oil of vitriol, it takes up a small quantity, which, however, is given up again on agitation with water. (Guibourt, *N. J. Pharm*, 11, 91; *comp.* Orfila, *N. J. Pharm*, 11, 10). — Ether mixes readily with *Bisulphide of Carbon.* On agitating this mixture with phosphorus, the phosphorus takes the sulphide of carbon from the ether, and dissolves in it, the solution forming a layer below the ether. (Böttger.) — Ether dissolves a small quantity of *Sulphide of Phosphorus*, forming a liquid which shines very brightly, like flame, when placed upon the hand, and from which the sulphide of phosphorus is not precipitated by water. (Böttger, *J. pr. Chem.* 12, 359.)

Ether dissolves *Iodine*, forming a brown solution, which, according to Solly, conducts electricity slightly. — Ether readily dissolves *Periodic acid.* (Beneckiser.)

It dissolves *Bromine*, forming a hyacinth-red solution (p. 185). This solution conducts electricity, but not so well as aqueous bromine. (Solly.)

It absorbs *Hydrochloric acid gas.* (Achard.) It likewise dissolves

in *aqueous hydrochloric acid*, without producing chloride of ether; hence water separates nothing from it. (Boullay.)

Ether, exposed to the air, absolves 0·15 vol. *Nitrogen* without any oxygen (Döbereiner, *Gilb.* 72, 432). — It absorbs *Nitrous gas*, and a large quantity of *Ammoniacal gas*.

Ether forms crystals with anhydrous *Potash* or *Soda*. These crystals are produced in the action of potassium or sodium upon ether (p. 189). On boiling Gay-Lussac's pyrophorus (obtained by igniting 1 pt. of sulphate of potash with 15 pts. of lamp-black) with anhydrous ether, and evaporating the liquid in dry air, crystals are likewise obtained, free from sulphide of potassium and deliquescing in damp air. (Kuhlman, *Ann. Pharm.* 33, 104.) — 1 pt. of hydrate of potash requires more than 25 pts. of ether to dissolve it (according to Connell, a much greater quantity still). The solution is yellowish, somewhat heavier than ether, and has a caustic taste. (Boullay.) — Ether does not dissolve baryta, strontia, or lime.

Ether dissolves crystallized *Chromic acid*. (Unverdorben.) It dissolves many *metallic Sulphides, Iodides, Bromides, Chlorides*, and *Fluorides*, as well as Oxygen-salts, but fewer and in smaller quantity than alcohol, and consequently precipitates many of these compounds from their aqueous solutions. (Vid. *Alcohol.*) — It absorbs gaseous *Fluoride of Silicium* abundantly, acquiring its peculiar odour. (Unverdorben, *N. Tr.* 9, 1, 32.) — It forms a yellow solution with *Chloride of Uranous oxide*. — Dissolves $\frac{1}{4}$ pt. of uranic nitrate, forming a yellow solution. (Bucholz.) For the decomposition of these solutions, under the influence of light, *vid.* pp. 187, 188. — Mixes with *Fluoride of Arsenic*, producing a slight rise of temperature. In glass vessels, the mixture becomes gelatinous, and deposits arsenious acid. (Unverdorben.) — With *Bichloride of Tin*, it forms a compound which crystallizes in feathery crystals, and distils at 80°. (Kuhlmann, *Ann. Pharm.* 33, 10.) These crystals are shining rhombic tables, which volatilize without decomposition, are decomposed by water, and dissolve readily in ether. They contain 23·14 per cent. C, 4·95 H. 8·61 O, 29·18 Sn, and 34·12 Cl, and are therefore: $2C^4H^5O,SnCl^2$. (Lewy, *Compt. rend.* 21, 371; abst. *J. pr. Chim.* 37,480.) — Ether dissolves a considerable quantity of *Sesquichloride of Iron*, forming a brownish yellow solution, and abstracts the greater quantity of that compound from its aqueous solution when agitated therewith. For the decomposition produced by light, *vid.* p. 188. *Protochloride of iron* is insoluble in ether; hence ether, shaken up with the aqueous solution of this compound, does not take up any of it, provided the air be excluded. (Jahn, *Ann. Pharm.* 19, 321.) — *Protochloride of Cobalt* dissolves sparingly in ether, forming a sky-blue liquid not decomposed by light. (Gehlen.) — *Dichloride of Copper* dissolves sparingly in ether, forming a colourless solution; *Protochloride of Copper* also not abundantly, forming a light yellowish green solution. (Gehlen, p. 188.) — 1 pt. of *Protiodide of Mercury* dissolves in 77 pts. of ether. (Saladin, *J. Chim. méd.* 7, 530.) — *Protobromide of Mercury* dissolves very abundantly. (Balard.) — 1 pt. of *Protochloride of Mercury* dissolves in 2·9 pts. of ether, whether cold or warm (J. Davy, *Phil. Trans.* 1822, 359; in 4 pts. (Karls); in 4·1 pts. (N. E. Henry.) — Ether abstracts protochloride of mercury from its aqueous solution. (Orfila.) The quantity which it abstracts, when shaken up with the aqueous solution, is greater as the solution is more concentrated. From a solution of 1 pt. corrosive sublimate in 20 pts. water, an equal volume of ether takes up 0·7 pts.; the remaining aqueous solution, again shaken

up with its own volume of fresh ether, gives up only 0·1 pt. to the ether. A solution of 1 pt. corrosive sublimate in 400 pts. water, agitated with 100 pts. of ether, loses only 0·3 pts. sublimate. (Lassaigne, *J. Chim. méd.* 13, 122.) The saturated solution of corrosive sublimate in ether has a density of 1·08, and does not deposit calomel when exposed to light. (J. Davy; compare, however, p. 188.) Phosphorus, immersed in the solution, throws down calomel and mercury. (Fengler, *Repert.* 9, 359.) — Ether readily dissolves hydrochlorate of *Terchloride of gold*; when shaken up with an aqueous solution of chloride of gold, it abstracts that compound, and floats in the form of a yellow stratum above the decolorized aqueous liquid, or, if more highly charged with chloride of gold, sinks below it. (Proust, *N. Gehl.* 1, 479.) For the decomposition by light, *vid.* p. 188. — Ether readily dissolves *Bichloride of Platinum;* the dark brown solution separates over-night into two layers, the upper of which is the thicker and paler; when exposed to sunshine, both layers lose their colour and unite. (Gehlen, *N. Gehl.* 1, 480.)

Ether mixes in all proportions with *Alcohol, Bisulphide of Methyl,* and *Methylal;* it dissolves *Sulphoform, Iodoform* (1 pt. iodoform to 7 pts. ether), *Bromoform, Protobromide of Carbon, Chlormethylase, Chloroform* (readily), and *Urea* (very sparingly); it likewise absorbs gaseous *Bromide of Methyl* (very sparingly), and *Chloride of Methyl* (more easily).

Ether absorbs 5 vol. *Cyanogen gas* (Gay-Lussac); mixes with *Hydrocyanic acid,* forming a liquid which boils even at the heat of the hand, and may be kept for a long time without decomposing (Ittner); mixes in all proportions with *Sulphocyanide of Methyl*; dissolves *Hydropersulphocyanic acid, Hydrozanthin,* and *Iodide of Cyanogen.*

It dissolves *Dichloride of Carbon.*

It absorbs its own volume of *Olefiant gas,* but gives off half of it on the addition of a large quantity of water. (Faraday).

Of the organic compounds yet to be considered, ether dissolves chiefly those which are comparatively rich in carbon and hydrogen, and poor in oxygen, — principally, therefore, volatile oils, resins, fats, alcohols, ethers of the second and third classes of the ethylene and amylene series; acetone and lignone, such of the acids and their salts as are comparatively poor in oxygen, even those which are insoluble in water,— also tannin, many colouring matters, and most of the alkaloids.

¶ Vino-methylic Ether. $C^6H^3O^2 = C^2H^3O, C^4H^5O$.

WILLIAMSON.—*Phil. Mag. J.* 37, 350; *Chem. Soc. Qu. J.* 4, 106; *Ann. Pharm.* 77, 49: *Laur. & Gerh. C. R.* 6, 354. — Further, *Chem. Soc. Qu. J.* 4, 229.

CHANCEL.—*Compt. rend.* 31, 152; *Laur. & Gerh. C. R.* 6, 369.

Ethylate of Methyl, Methylate of Ethyl (Williamson); *Vinométhylide.* (Chancel.)

Formation. 1. By the action of iodide of methyl on ethylate of potassium or sodium ($C^4H^5KO^2$), or of iodide of ethyl on methylate of potassium. (Williamson.)

$$\left.\begin{array}{r} C^4H^5KO^2 + C^2H^3I \\ \text{or: } C^2H^3KO^2 + C^4H^5I \end{array}\right\} = KI + C^6H^8O^2.$$

2. By the action of sulphomethylate of potassium on ethylate of potassium. (Chancel.)

$$C^4H^5KO^2 + C^2H^3KO^2,2SO^3 = 2(KO,SO^3) + C^6H^8O^2.$$

Preparation.—By distilling iodide of ethyl with methylate of sodium. [This is preferable to the inverse process of distilling iodide of methyl with ethylate of sodium, because the higher boiling point of the iodide of ethyl renders it easier to remove any excess of it by distillation.] The alcohols used in the preparation of these two compounds must be as anhydrous as possible, and the naphtha which surrounds the sodium must be removed completely by drying with bibulous paper and subsequent immersion for a few seconds in a small portion of absolute alcohol, which serves successively to rinse all the pieces of metal used in one experiment. The pieces of sodium thus purified are thrown, one at a time, into the methyl-alcohol until the liquid is completely saturated with sodium. The solution, after cooling, is mixed with iodide of ethyl — whereupon a precipitate of iodide of sodium is formed — and distilled, the compound ether passing over, together with vapour of methylic alcohol and some of the iodide. To remove these admixtures, the distillate is treated with sodium (or, better, with potassium, because it acts more strongly), which, as long as any methylic alcohol is present in equivalent quantity with the iodide of ethyl, forms more of the compound ether; and, when all the iodide has thus been decomposed, forms, with the remaining alcohol, methylate of potassium or sodium, from which the ether may be distilled off in the pure state. To render the action of the metal more complete, it is best to arrange the distilling apparatus in such a manner that the distillate may constantly flow back again into the retort until all action has ceased, and then to distil off the ether from the fixed products of the action. As this ether boils at a very low temperature, and in fact can only be retained in the liquid state either by inclosing it in a sealed tube or by surrounding it with a freezing mixture, it may be distilled by simply removing the freezing mixture from the body of the retort. (Williamson.)

Transparent, colourless, very mobile liquid. Boils at 11°. Vapour-density, 2·158. (Williamson.) The vapour is highly inflammable, and has a peculiar ethereal odour. (Chancel.)

			Williamson.	Or:	
6 C	36	60·00	59·39	3 C	18
8 H	8	13·33	13·46	4 H	4
2 O	16	26·67	27·15	O	8
$C^6H^8O^2$	60	100·00	100·00	C^3H^4O	30

	Vol.	Density.	Or:	Vol.	Density.
C-vapour	6	2·4960	C-vapour	3	1·2480
H-gas	8	0·5536	H-gas	4	0·2768
O-gas	1	1·1092	O-gas	½	0·5546
Vapour of $C^6H^8O^2$	2	4·1588	Vapour of C^3H^4O	1	2·0794
	1	2·0794			

According to the atomic weights adopted by Williamson & Chancel, the formula of this ether is C^3H^8O, $= \left.\begin{matrix}CH^3\\C^2H^5\end{matrix}\right\}O$, and it may be regarded as water in which 1 At. H is replaced by methyl and the other by ethyl. (*Comp.* p. 177; also VII, 17, 191. — According to the atomic weights adopted in this Handbook, the formula might be reduced to C^3H^4O, which would represent the compound as containing, not ethyl and methyl, but a new radical, C^3H^4. ¶

Alcohol. $C^4H^6O^2 = C^4N^4, H^2O^2$.

TH. SAUSSURE. Composition. *J. Phys.* 64, 316; also *N. Gehl.* 4, 48; also *Gilb.* 29, 118 and 268. — *Ann. Chim.* 89, 273; also *J. Phys.* 78, 115; also *A. Tr.* 25, 2, 384.

GAY-LUSSAC. *Ann. Chim.* 95, 311.

JEAN DUMAS & POLYDORE BOULLAY. Decomposition by Sulphuric acid. *Ann. Chim. Phys.* 36, 294; also *J. Pharm.* 14, 1; also *Schw.* 52, 75; also *Pogg.* 12, 93.

HENNELL. Decomposition by Sulphuric acid. *Phil. Trans.* 1828, 365; also *Ann. Chim. Phys.* 42, 77; also *Pogg.* 14, 233; also *N. Tr.* 21, 224.

SERULLAS. Decomposition by Sulphuric acid. *Ann. Chim. Phys.* 39, 152; also *Schw.* 55, 147; also *Pogg.* 15. 20.

DUFLOS. *Kastn. Arch.* 12, 129; 14, 291.

KUHLMANN. Decompositions and Combinations. *Ann. Pharm.* 33, 97, and 192.

LIEBIG. Decomposition by Chlorine. *Ann. Pharm.* 1, 182; also *Pogg.* 24, 243. — Ether-theory. *Ann. Pharm.* 9, 1; also *Pogg.* 31, 320. — Etherification. *Ann. Pharm.* 23, 39; 30, 129. — *Handworterb.* 1, 110.

MAGNUS. Decomposition by Sulphuric acid. *Pogg.* 27, 367.

H. ROSE. Etherification. *Pogg.* 48, 463.

ARTHUR CONNELL. Decomposition by Electricity. *Transact. of the Roy. Soc. of Edinb.* 13, 315; also *J. pr. Chem.* 5, 168; abstr. *N. Ed. Phil. J.* 19, 159; abstr. *Pogg.* 36, 487. — *Transact. of the Roy. Soc. of Edinb.* 14, 159. — *Phil. Mag. J.* 18, 47, 241, and 353; also *J. pr. Chem.* 25, 275 and 279.

ZEISE. Decomposition by Chloride of Platinum. *Pogg.* 21, 497, and 542.

MASSON. Decomposition by Chloride of Zinc. *Ann. Chim. Phys.* 69, 225.

R. F. MARCHAND. *J. pr. Chem.* 15, 1.

GRAHAM. Crystalline compounds of Alcohol. *Phil. Mag. Ann.* 4, 265 and 331; also *Schw.* 55, 180; also *Repert.* 34, 426; abstr. *Pogg.* 15, 150. — Etherification. *Chem. Soc. Qu. J.* 3, 24; *Ann. Pharm.* 75, 108; *N. J. Pharm.* 18, 124; abstr. *Pharm. Centr.* 1850, 826; *Jahresber.* 1850, 456.

WILLIAMSON. Etherification. *Phil. Mag. J.* 37, 350; *Chem. Soc. Qu. J.* 4, 106; *Ann. Pharm.* 77, 37; *J. pr. Chem.* 52, 336; *Pharm. Centr.* 1851, 129. — *Laur. & Gerh. Compt. rend.* 1850, 354; *N. J. Pharm.* 19, 15; *Jahresber.* 1850, 459. — *Chem. Soc. Qu. J.* 4, 229; *Ann. Pharm.* 81, 73; *J. pr. Chem.* 55, 257; *Jahresber.* 1851, 510.

CHANCEL. Etherification. *Laur. & Gerh. C. R.* 1850, 369; *Compt. rend.* 31, 521; *J. pr. Chem.* 51, 316; *Pharm. Centr.* 1851, 132; *Jahresber.* 1851, 461.

Spirit of Wine, Hydrated Oxide of Ethyl; Alkohol, Weinalkohol [Lenevine]; Alkohol Vini, Spiritus Vini; Alcool, Esprit de Vin.

History. Fermented drinks, such as wine and beer, have been known from the earliest times. The Greeks and Romans were not acquainted with the mode of separating the alcohol from these liquids, a process which appears not to have been practised till later times, by the northern nations. Abucasis, in the twelfth century, showed how to obtain spirit from wine; Raimund Lullius, in the thirteenth century, first dehydrated it

partially by means of carbonate of potash; afterwards Lowitz effected the complete dehydration; Stahl regarded it as a light oil combined with acid and water; Junker, as phlogiston united with acid and water. Lavoisier pointed out its peculiar composition, which was quantatively determined by Saussure.

Formation. — Only by *Vinous Fermentation*, i. e., by the decomposition which sugar undergoes in contact with ferment and water at a certain temperature, and by which it is converted into alcohol and carbonic acid, the latter escaping as gas. (Vid. Vinous Fermentation.)

Preparation. 1. Of *Hydrated Alcohol.* — By distilling liquids which have undergone the vinous fermentation, such as wine, beer, or brandy till the liquid which passes over no longer contains alcohol. The distillate, which still contains a very large quantity of water, if again distilled till nothing but water passes over, yields *Brandy;* this is converted by another fractional distillation into *Rectified Spirit of Wine;* and this, by similar treatment, into the *most highly rectified spirit.* For the alcohol being more volatile than water, passes over first; and the residue of the distillation is water, containing small quantities of acetic acid and fusel-oil.

At the present day, very strong alcohol is obtained at the first distillation of wine or brandy by the process of Ed. Adam. (*Gilb.* 32, 129.) A very complicated copper apparatus is used, consisting of a number of connected vessels, only the first of which is heated, and the vapours thence evolved are passed successively into the other vessels, which are partly filled with liquid obtained in a former distillation, and of continually increasing strength as they are further from the still, the last however being empty. By this arrangement the watery vapour condenses chiefly in the vessels nearest the still, while an alcohol-vapour containing continually less water passes into the following vessels; this vapour, after it has passed through all the vessels, and deposited the greater part of its water, is condensed in the cooling tube (*vid.* Hermbstädt, *Kunst Branntwein zu brennen*, Berlin). To obtain strong spirit at the first distillation from watery liquids containing but little alcohol, on the small scale, they may be boiled, on the principle of Adam's method, in a flask, having a glass tube fitted to it by means of a cork. This tube passes vertically upwards to the height of 2 inches, then slightly inclined upwards for 3 feet, then slightly downwards for 2 feet; it is surrounded with paper which is kept moist, and passes into a cooled flask which serves as a receiver.

Alcohol is generally contaminated with small quantities of *Acetic acid* and various kinds of *Fusel-oil*, which impart to it a peculiar odour, varying according to their source. The acetic acid, being less volatile than alcohol, remains for the most part, together with a large portion of the fusel-oil, in the residues of the several distillations, and the last portions of the acid may be separated from the alcohol by distillation over a small quantity of carbonate of potash or ash. But the several kinds of fusel-oil (potato-oil, fusel-camphor, œnanthic ether, and probably others also, are difficult to separate completely). For the *defusellation* of alcohol, the following processes are used:

1. The alcohol is distilled, after addition of a small quantity of water; the first distillate, which contains the least fusel-oil, being collected apart, and subjected several times to the same kind of fractional distillation with

water. For the fusel-oil, being less volatile, passes over chiefly towards the end of the distillation, and yields, when nearly all the alcohol has passed over, a turbid distillate, because the alcohol which distils over at that stage of the process contains too much water to hold the fusel-oil in solution. The head and condensing tube must be cleaned after each distillation; otherwise the alcohol which passes over at the beginning of the following distillation will be strongly contaminated by the fusel-oil deposited in them. In an apparatus arranged on Adam's principle, this cleansing may be effected by a single distillation.

2. Spirit of the strength of 60 to 80 per cent. is placed for several days in contact with charcoal-powder, and frequently agitated, after which it is decanted from the charcoal and rectified. The charcoal mixed with water and distilled, yields an additional quantity of alcohol, but impure, because at the heat required for the distillation, it gives up part of the fusel-oil which it has absorbed. The softer the charcoal, the more active is it. 1 pt. of fir-charcoal burnt in the *meiler* is as efficient as 4 pts. of oak-charcoal and 7 pts. of bone-charcoal. (Lüdersdorf, Giesecke, *N. Br. Arch.* 28, 339.) For purifying wine-brandy, bone-charcoal is preferable to wood-charcoal. (Stickel, *Repert.* 58, 91.)

3. Weak spirit is distilled over almond-paste. (Mayr, *Br. Arch.* 32, 249.) Sweet oil of almonds or bruised sweet almonds, which were formerly recommended, are too costly.

4. It is mixed with a small quantity of milk and salt, and distilled over oak-shavings. (Schütz, *Repert.* 15, 275.)

5. Brandy is mixed with an equal quantity of water, and 256 parts of the mixture distilled over 1 pt. of *Magnesia alba.* (Zanon, *Repert.* 57, 131.) Very good; but the spirit should be left for some time in contact with the magnesia (calcined magnesia is best) and shaken up, then filtered and distilled. (Pfeffer, *Repert.* 65, 95.)

6. The spirit is distilled over caustic potash, best with addition of charcoal-powder. (Göbel, *Schw.* 63, 225.) This method is useful for potato-brandy and grain-brandy, but not for wine-brandy. (Stickel.)

7. The spirit is filtered through a layer of powdered quicklime. (Ficinus, *J. pr. Chem.* 8, 410.)

8. Brandy is distilled over a small quantity of chloride of lime. To 1 pt. of bleaching powder, previously triturated with water to a paste, about 664 pts. of brandy are added, and distilled after 24 or 48 hours. If the quantity of chloride of lime is too small, fusel-oil remains undecomposed; if too large, certain products of the decomposition of alcohol by chloride of lime pass over. (Zeise, *N. Trs.* 7, 1, 145.) The residue still smells of fusel-oil, consequently the distillation must not be continued too long. (Schwacke, *Br. Arch.* 38, 202.) Chloride of lime serves also for removing fusel-oil from wine-brandy, for which all the other means, excepting the use of charcoal, are useless. (Stickel.)

9. Brandy is distilled over a small quantity of mineral chameleon. (*J. Chim méd.* 0, 568.) The odour of the fusel-oil is then replaced by another, which is not unpleasant. (Hopff, *Repert.* 56, 67.— *Comp.* also Döbereiner, *Jahrb. d. pr. Pharm.* 6, 93.)

The presence of fusel-oil in alcohol may be recognized by the taste, especially after dilution with a large quantity of water; and by the odour, especially after rubbing it between the hands, or letting it partially burn away. Alcohol free from fusel-oil should remain clear when mixed with nitrate of silver and exposed to sunshine; but spirit of wine and wine-brandy containing fusel-oil assume a faint red tint, and brandy from cider

or potatoes becomes strongly reddened. (A. Vogel, *Kastn. Arch.* 15, 100.) — When a solution of 1 pt. hydrate of potash in a small quantity of water is mixed with 160 pts. of brandy or spirit of wine containing fusel-oil, the mixture, after agitation, slowly evaporated to 15 pts., and the residue mixed in a stoppered bottle with 15 pts. of dilute sulphuric acid, there is evolved, in the case of potato-brandy, a vapour having a very disgusting odour, and producing when inhaled, constriction of the throat, head-ache, and giddiness; in the case of grain-brandy, a vapour having a disagreeable odour somewhat like that of sour dough, and a similar but less powerful action; and in the case of rum, arrack, and wine-brandy different, but always specific odours. In this manner, the origin of any sample of spirit not perfectly deprived of fusel-oil may be recognized, even when no particular odour can be detected by ordinary examination. Even different wines, when evaporated with potash and treated with sulphuric acid, emit peculiar odours, by which they may be distinguished one from the other. (Göbel, *Schw.* 63, 225.)

II. Of *Dehydrated* or so-called *Absolute Alcohol.* — Mere fractional distillation, however often repeated, never suffices to free alcohol completely from water; for although alcohol boils at 78°, its vapour nevertheless takes up by adhesion a quantity of aqueous vapour corresponding to this temperature (I. 266). Hence the most highly rectified spirit, or ordinary alcohol obtained by repeated distillation, still exhibits a density of 0·820 to 0·830. The complete dehydration of alcohol is effected by one of the three following methods:

1. By distilling the most highly rectified spirit over fixed substances which have a strong tendency to retain the water.

In this distillation, it is best to use, not a retort, but a still with head and condensing tube (Schroder, *N. Tr.* 1, 165), or on the small scale, a flask with a long bent glass tube (*App.* 51), so that nothing may be lost by spirting.—By this process, if carbonate of potash or chloride of calcium be used, the nature of the alcohol is not altered and no ether is produced. (Saussure.)

a. *Carbonate of Potash.* Highly rectified spirit is shaken up with ignited carbonate of potash, which forms a watery layer beneath the alcohol, or, at least, becomes pasty. The alcohol, whose density is then 0·815, is poured off into a distilling vessel containing twice the quantity of pulverized and recently ignited carbonate of potash, left to stand for 24 hours, and then $\frac{2}{3}$ of it distilled off. (Lowitz. *Crell. Ann.* 1796, 1, 195.)

b. *Chloride of Calcium* fused or heated nearly to its melting point. — Equal parts of chloride of calcium and alcohol of sp. gr. 0·830 to 0·835 are digested, with agitation, till the chloride of calcium is dissolved; any alcohol that may have passed over is poured back; and then half distilled off. (Richter, *Crell. Ann.* 1796, 211; *N. Gegenst.* 8, 67.) — The residue serves for the partial dehydration of fresh alcohol. The last portions of alcohol may be separated from the residue by adding water and distilling. — One distillation over chloride of calcium does not render the alcohol absolute. 4 parts of the most highly rectified spirit should therefore be distilled with 3 pts. chloride of calcium till 3 pts. have passed over; and these 3 pts. of spirit of sp. gr. 0·80, distilled over $2\frac{1}{4}$ pts. chloride of calcium, at the rate of a drop in two seconds, till 2 pts. of absolute alcohol have passed over, having a density of 0·795 at 15·5° C. (60° F.) The process should be performed with small quantities only; if large quantities

2. By placing hydrated alcohol under an exhausted receiver, together with a substance having a strong attraction for water.

a. If *chloride of calcium* be used, the strength of alcohol increases in 4 days by 5° to 8° Bm.; and if the chloride of calcium be often renewed, the alcohol may be brought to 40° or 42° Bm. (Pajot Descharmes, *Ann. Chem. Phys.* 29, 328; also *N. Tr.* 12, 1, 302.)

b. With 4 ounces of alcohol of sp. g. 0·827, and 9 ounces of powdered *quicklime* spread out in a basin, 5 days are required in summer and 8 in winter to lower the density to 0·796 at 15·5°, beyond which it will not diminish any further. Oil of vitriol or chloride of calcium cannot be used, because it would absorb the alcohol as well as the water. (Graham). If the lime be renewed every week, the alcohol, after 4 weeks, exhibits, at 15·5°. a density of 0·795, and after 12 weeks of 0·7938, which is equivalent to 0·790 at 20°. (A. Connell, *N. Edinb. Phil. J.* 19, 162; also *J. pr. Chem.* 5, 205.)

3. When hydrated alcohol is placed in a bladder and exposed to warm air, the water gradually evaporates through the bladder, and ultimately leaves the alcohol anhydrous. (Sömmering.) For further observations on this matter, vid. *Hydrated Alcohol.*

Alcohol, at least when distilled over chloride of calcium, may, with various degrees of facility according to its origin, be brought to a density of 0·791 at 20°. Wine-brandy is easily brought to this state; but grain-brandy cannot be brought lower than 0·793 or 0·792, a circumstance which seems to indicate the existence of impurities (fusel-oil) (Meissner).

Alcohol may be regarded as perfectly anhydrous, if sulphate of copper previously burnt white and immersed in the alcohol in a close vessel, does not recover its blue colour. (Casoria.)

Properties. Transparent, colourless, very thin liquid. When exposed to a very great degree of cold, it becomes viscid but does not solidify. Alcohol of sp. gr. 0·798 cooled to —90° by solid carbonic acid, becomes oily and viscid, and at —99° resembles melted wax; but alcohol of sp. gr. 0·820 solidifies at this temperature. (Mitchell, *Sill. Am. J.* 1840, 177; also *Ann. Pharm.* 37, 356.) ¶. Despretz (*Compt. rend.* 28, 143), observed that absolute alcohol, surrounded by liquid nitrous oxide, and likewise, on all sides by a mixture of solid carbonic acid and ether, became viscid under an exhausted receiver, and on one occasion even appeared to solidify on the surface ¶.—For Hutton's imaginary statements respecting the freezing of alcohols at —79° vid. *Schw.* 19, 301.

Specific gravity of alcohol: 0·791 (Lowitz); 0·792 (Richter); 0·791 at 20°, or 0·793 at 17·5° (Meissner); 0·7925 at 18° (Dumas & Boullay); 0·7996 at 15°, and 0·81796 at 0° (Kopp); 0·7938 at 15·5°, 0·7928 at 16·8°, and 0·790 at 20° (Connell); 0·8151 at 0° (Pierre); 0·7938 at 15·6° (Fownes). — Boiling point: 78·41° at 0·76 met. pressure (Gay-Lussac); 76° at 0·745 met. (Dumas & Bouillay); 77·25° at 26″ 7·8‴ (Yelin); 78·6° (R. F. Marchand); 78·8° at 27″ 9·1‴, when a platinum wire is immersed in it, so that the bubbles rise from the surface of the wire; according to another observation, 78·4° at 0·76 met. (Kopp); 78·3° at 0·758 met. (Pierre); 77·9° at 0·76 met. (Andrews); 78·4° (Person). — Tension of vapour, according to Ure (I. 262, 263); according to Dalton: 0·56 English inches of mercury at 2·2°; 1·51 in. at 17·8°; 4·07 in. at 35·5°; 11 in. at 55·5°; 29·7 in. at 78·3°; and 80·2 in. at 104·5°. — Vapour-density: 1·6133 (Gay-Lussac; 2·1 (Dalton). — Refracting power of the vapour (I .95\—

Alcohol is a very bad conductor of electricity. Its enlivening odour, burning astringent taste, and intoxicating action are well known.

			Saussure.	Dumas & Boullay.	Ure. sp. gr. 0·812.	Macaire & Marcet. sp. gr. 0·820.
4 C	24	52·18	51·98	52·37	47·85	48·8
6 H	6	13·04	13·70	13·31	12·24	11·3
2 O	16	34·78	34·32	34·61	39·91	39·9
$C^4H^6O^2$	46	100·00	100·00	100·29	100·00	100·0

	Vol.	Density.		Vol.	Density.
C-vapour	4	1·6640	Ethylene-gas	1	0·9706
H-gas	6	0·4158	Vapour of Water	1	0·6239
O-gas	1	1·1093			
Alcohol-vapour	2	3·1891		1	1·5945
	1	1·5945			

Respecting the constitution of alcohol, compare the observations already made on that of ether (p. 176). According to the system adopted in this work, it is regarded as ethylene, C^4H^4, to which are attached 2H and 2O, but not combined in the form of water, — or rather, perhaps, as C^4H^3O,H^3O (VII. 32 to 35). According to Dumas & Boullay, it is C^4H^4+2Aq; according to the ethyl-theory, it is the hydrated oxide of ethyl= C^4H^5O+Aq, containing, therefore, 1 At. water already formed. Malaguti (*Ann. Chim. Phys.* 70·400), gives the preference to the formula C^4H^3O,H^2+Aq. according to which it is formed from ether, C^4H^3O,H^2, by the addition of 1 At. water. — ¶. According to Williamson, Chancel, and Gerhardt, alcohol is water in which 1 At. H is replaced by ethyl, so that, adopting Gerhardt's atomic weights, given on page 28, vol. VII, its rational formula is $\left.\begin{matrix}C^2H^5\\H\end{matrix}\right\}O$; (*vid.* VII. 17, 18; also *Etherification*, p. 236, of this volume). ¶

That alcohol is a hydrate of ether or oxide of ethyl, appears from the following considerations: Substances which absorb water or its elements with avidity, such as fluoride of boron or chloride of zinc, convert alcohol into ether when they are heated with it; other bodies, such as sulphuric acid, decompose the hydrate of ether by abstracting the ether. The electric current eliminates hydrogen gas at the negative pole, formed by the decomposition of the water contained in the alcohol. (Liebig, *Ann. Pharm.* 9, 1; 19, 270; 23, 24.) — These and similar reasons do not, however, compel us to admit the existence of ready-formed water in absolute alcohol. On the other hand, the fact adduced by Mitscherlich (*N. Ann. Chim. Phys.* 7, 12), that the solution of ether in water does not produce dilute alcohol, is unfavourable to such a supposition. H. Rose (*Pogg.* 48, 468), indeed, compares ether with an ignited oxide, which no longer forms a hydrate when brought in contact with water. Such an oxide, however, remains quite unaltered in the water, whereas the ether dissolves. (*comp.* also Laurent, *Rev. scientif.* 14, 333.) If alcohol were a hydrate of ether, substances which have a strong attraction for water should in other respects act upon alcohol and ether in the same manner. But anhydrous sulphuric acid, besides forming isethionic acid and hydrated sulphuric acid, forms oil of wine with ether; but with alcohol, not a trace of wine-oil, but sulphate of carbyl, $C^4H,4SO^3$. (Magnus, 47, 509.)

Decompositions. 1. *By a red heat.* Alcohol-vapour, passed through a red-hot glass or porcelain tube, yields carbonic oxide, water, hydrogen, marsh-gas, olefiant gas, naphthaline, empyreumatic oil, and charcoal. The products vary according to the temperature and the nature of the tube, also according to the substances contained within it. The above-mentioned products may be formed in the manner represented by the following equations:

Carbonic oxide, hydrogen, and marsh-gas:

$$C^4H^6O^2 = 2CO + 2H + C^2H^4.$$

Carbonic oxide, hydrogen, and olefiant gas:

$$2C^4H^6O^2 = 4CO + 8H + C^4H^4.$$

Hydrogen gas and aldehyde:

$$C^4H^6O^2 = C^4H^4O^2 + 2H.$$

At a higher temperature, the marsh gas and olefiant gas may deposit charcoal, and form small quantities of other hydrocarbons, such as naphthaline and oil, containing a larger number of carbon-atoms. (VII. 43.)

Alcohol vapour does not undergo decomposition at 300° in a tube filled with fragments of porcelain; but it gives off gas even at 220°, if the tube contains spongy platinum. (Reiset & Millon, *N. Ann. Chim. Phys.* 8, 290.) — Alcohol remains unaltered when heated to 240° in a sealed glass tube, either with or without chloride of calcium. (Magnus.)

Alcohol vapour passed through a red-hot empty glass tube, yields neither empyreumatic oil nor charcoal, but (together with undecomposed alcohol) a gas of sp. gr., 0·436, which burns with a pale flame like that of alcohol, does not form Dutch liquid when mixed with olefiant gas in the dark, or yield olefiant gas when passed through a red-hot pipe-tube. But if the glass tube contains fragments of an earthen pipe, or alumina, or silica (lime, magnesia, sulphate of potash, and charcoal, are without action upon it), or if an earthen pipe be used, which can be surrounded with a glass tube, a gaseous mixture is obtained, from which chlorine in the dark condenses a large quantity of olefiant gas in the form of oil, leaving a residual gas which burns merely with a bluish flame. (Deiman, &c. *Crell. Ann.* 1795, 2, 312, and 430.)

Alcohol vapour passed through a tube filled with pieces of glass does not decompose at 130°, but at a dull red heat yields aldehyde, water, and a combustible gas. (Marchand, *J. pr. Chem.* 15, 7.)

81·37 grammes of alcohol of sp. gr. 0·832 at 17° (containing, therefore, 11·23 grammes of water), passed slowly in the state of vapour through a red-hot porcelain tube, yields: *a.* Deposited in the tube; 0·05 grm. carbon; *b.* In the long glass tube connected with it, and surrounded with ice; 0·41 grm. of oil, partly liquid, partly crystallized in delicate laminæ (naphthalin, according to Reichenbach); *c.* In the tubulated receiver connected therewith: 17·24 grm. of colourless water, containing 0·65 grm. undecomposed alcohol, and 0·05 grm. acetic acid; *d.* In a bell-jar, closed at the bottom with water, under which there dips a gas-delivery tube proceeding from the receiver, and passing under the jar: a gaseous mixture which, in the moist state, at 11·25°, and under a pressure of 0·7257 met., measures 87·07 litres, and weighs 60·25 gr. This gas contains no carbonic acid, or at most ½ per cent.; and 100 volumes of it exploded with oxygen gas consume 122 vol. oxygen, and produce 81·15 vol. carbonic acid. (Saussure.) Calculating from these data, and according to the rules given on page 251, Vol. VII, we find that 100 volumes of the gaseous mixture contain of hydrogen,

$100 - 81{\cdot}15 = 18{\cdot}85$ vol.; of marsh-gas: $\frac{(2\ .\ 122) - 100}{3} = 48$; and of carbonic oxide: $81{\cdot}15 - 48 = 33{\cdot}15$. The specific gravity of a mixture of 18·85 vol. hydrogen gas, 48 vol. marsh-gas, and 33·15 carbonic oxide, is by calculation, 0·601. Saussure found that one litre of the gas which he obtained weighed 0·75804 grm. in the dry state at 0° and under 0·76 met. pressure; hence the specific gravity is 0·584, a result agreeing tolerably well with the preceding.

Hydrated alcohol passed through a tube at a low red heat, yields but little naphthalin; but absolute alcohol passed through a white-hot tube, yields a large quantity of naphthalin in colourless needles and laminæ, together with a considerable quantity of brown empyreumatic oil. (Reichenbach, *Schw.* 61, 493.)

Compare also Priestley (*Natur. Phil.* 3, 146) and Vauquelin, (*Fourcroy, Syst.* 8, 155) who spoke of the naphthalin crystals as a concrete volatile oil.

¶ Berthelot (*N. Ann. Chim. Phys.* 33, 295) has also examined the products obtained by passing alcohol vapour through a red-hot porcelain tube filled with fragments of pumice-stone; the products of the decomsition were collected in cooled vessels containing various reagents. Among them were found: Naphthalin; benzol (which, by being passed into fuming nitric acid, was converted into nitrobenzol); phenol; acetic acid ?; aldehyde; a yellowish solid substance, whose ethereal solution exhibited dichroism of yellow and blue; a yellowish brown substance having an alliaceous odour something like that of the oils contained in wood-spirit, and consisting of a solid and a liquid body mixed together. The evolved gases consisted of olefiant gas, which formed a third of the whole, and of hydrogen, carbonic oxide, and probably marsh-gas; they smelt very much like sea-fish. ¶

2. *Electricity.* Anhydrous alcohol completely stops the current of a weak galvanic battery, but in the circuit of a battery consisting of many pairs of plates, it very slowly gives off hydrogen at the negative pole, the current being at the same time greatly weakened, so that the magnetic needle is but slightly affected. No gas is evolved at the positive pole, but a resin is formed there, which remains behind when the liquid is evaporated. (Connell.)

If two parallel platinum plates be introduced as electrodes into alcohol of sp. gr. 0·790 at 20°, their surfaces being from $\frac{1}{49}$ to $\frac{1}{36}$ of an inch apart, and the current of a battery of 216 pairs of 4-inch plates made to act on the liquid, no gas is evolved at the positive pole, but hydrogen escapes very slowly at the negative pole. — In alcohol of sp. gr. 0·7928 at 18·9°, if the plates are from $\frac{1}{30}$ to $\frac{1}{20}$, or even $\frac{1}{10}$ of an inch apart, hydrogen gas will still be evolved under the influence of a current of the same strength; the quantity evolved is, indeed, somewhat greater than in the former case, but yet amounts to only 0·2 or 0·3 of an inch in an hour. At the beginning of the action, the alcohol boils for a while. The evolved gas is pure hydrogen (not olefiant gas, as stated by Richter) mixed only with a small portion of air which had been absorbed by the alcohol. After an hour's action, the alcohol exhibits an ethereal odour, and when mixed with a little water and evaporated, leaves a small quantity of yellow resin. If the same alcohol be subjected to the action of 72 pairs of 4-inch plates, the evolution of gas continues under the same circumstances for only a minute or two, and the alcohol merely becomes warm, but does not boil; even with 50 pairs, a slight evolution of gas is *perceptible, but it* lasts only a minute or two. (Connell.)

When a current from 80 pairs of plates, each having a surface of 16 square inches, acts by means of two platinum wires $\frac{1}{10}$ of a line apart, upon alcohol of sp. gr. 0·789, sparks appear at first, and a combustible gas is evolved at the negative pole; but the alcohol appears to remain unaltered. (Lüdersdorff, *Pogg.* 19, 77.)

The more dilute the alcohol, the less resistance does it offer to the passage of the current, and the greater is the quantity of hydrogen evolved at the negative pole; when the quantity of water present is comparatively large, oxygen is likewise evolved at the positive pole, but its quantity is very small in comparison with that of the hydrogen. Aldehyde, acetic acid, and other products of decomposition, appear to be produced at the same time.

Alcohol of sp. gr. 0·809, exposed to the current of an 80-pair battery, gives off a large quantity of gas at the negative pole, but nothing at the positive pole; after 8 days' action, it acquires the odour of fenugreek, and of the flowers of *Saponaria off.*, and reddens litmus. Alcohol of sp. gr. 0·818 to 0·984 gives off gas still more abundantly, but only at the negative pole, and smells and tastes very much like nitrous ether; when distilled, it yields a liquid smelling strongly of ether, perhaps containing oxygen-ether [aldehyde], and leaves acetic acid. If the positive pole consists of zinc or lead, the metal becomes oxidized, and the alcohol remains unaltered. (Lüdersdorff, *Schw.* 33, 622; further, *Pogg.* 19, 77.)

Hydrated alcohol gives off hydrogen under the influence of a weaker current than absolute alcohol does, and a mixture of alcohol and water in equal parts, likewise gives off a gas at the positive pole, but in very small quantity. Alcohol of sp. gr. 0·830, exposed to the current of 50 pairs of 4-inch plates, with platinum poles $\frac{1}{10}$ of an inch apart, gives off but a small quantity of gas at the negative pole, and only when heated nearly to the boiling point. (Connell.)

The addition of iodine, acids, alkalis, metallic iodides, chlorides, and oxygen-salts, likewise increases considerably the decomposibility of alcohol by the electric current, besides giving rise to peculiar phenomena.

Alcohol containing iodine does not give off hydrogen at the negative pole under the influence of a battery of 50 pairs of 2-inch plates. (Connell.)

Alcohol containing sulphurous or sulphuric acid acquires a strong alliaceous odour when acted upon by the electric current. (Lüdersdorff.) [xanthic acid ?].

Small quantities of boracic or arsenic acid facilitate the decomposition of absolute alcohol and the evolution of hydrogen at the negative pole. (Connell.)

A mixture of 2 vol. alcohol, 1 vol. water, and a small quantity of phosphoric acid, placed in the circuit of a small 16-pair battery, the positive pole of which consists of recently ignited spongy platinum, gives off a large quantity of hydrogen at the negative pole, but at the positive pole only a few bubbles of oxygen at the beginning, and only when this pole is immersed in the liquid after the negative pole; but if a platinum wire be used as the positive pole instead of spongy platinum, an evolution of oxygen takes place. The spongy platinum, after the experiment, smells like acetal; moreover, aldehyde, acetic acid, formiate of ethyl, and acetate of ethyl, appear to be produced. The odour of acetal is apparent, even when a considerable quantity of water is present. A mixture of 2 vol. alcohol, 1 vol. water, and 1 vol. sulphuric acid, behaves in a similar manner. A

mixture of equal volumes of alcohol and nitric acid of sp. gr. 1·35, gives off no gas at either of the electrodes if they consist of recently ignited spongy platinum; if platinum wires be used, only the negative pole gives off gas, little or none being given off at the positive pole. With equal measures of alcohol, nitric acid and water, the negative spongy platinum gives off hydrogen; while little or no gas is evolved at the positive pole, whether it consists of spongy platinum or of platinum wire. In a mixture of 1 vol. alcohol, 1 vol. water, and 6 vols. nitric acid, the negative spongy platinum gives off a large quantity of gas, but the positive pole yields no gas if it consists of spongy platinum, a small quantity if it consists of platinum wire, more if it consists of gold wire, and a large quantity of oxygen if it consists of iron wire. Hence it appears that platinum facilitates the action of nascent oxygen upon alcohol, whereas passive iron does not. (Schönbein, *Pogg.* 47, 563.)

A mixture of alchohol and ammonia in equal parts is converted, in the voltaic circuit, into a liquid, which is no longer inflammable, has an offensive odour and bitter taste, and leaves a fatty residue when evaporated. (Lüdersdorff.)

Alcohol containing potash yields at the positive pole the same resin [resin of aldehyde] that is produced by treating aldehyde with potash. (Döbereiner, *Pogg.* 24, 609.)

Alcohol of sp. gr. 0·790, which, when exposed in the pure state to the current produced by 216 pairs of 4-inch plates, with electrodes of platinum-foil placed between $\frac{1}{40}$ and $\frac{1}{30}$ of an inch apart, gives off very little gas, yields a larger quantity when only $\frac{1}{10,000}$ pt. of hydrate of potash is dissolved in it; with $\frac{1}{1000}$ of potash-hydrate, 72 pairs of 4-inch plates, with platinum-poles $\frac{1}{20}$ of an inch apart, produce half a cubic inch of hydrogen gas in 10 minutes; with $\frac{1}{200}$ potash-hydrate, they make the alcohol boil for a while, and yield 1 cub. in. hydrogen (not olefiant gas) in 15 minutes. Alcohol of sp. gr. 0·835...0·840, in which $\frac{1}{100}$ pt. of potash-hydrate is dissolved, yields at first a small quantity of oxygen gas, amounting to only $\frac{1}{10}$ of the hydrogen evolved. This evolution of hydrogen is accompanied by deposition of carbonate of potash at the negative pole, and the formation of a large quantity of resin, which imparts to the liquid first a light and then a dark red colour, and may be obtained in the form of a precipitate by dissolving the residue in water, and adding hydrochloric acid. (Connell.)

The quantity of hydrogen gas evolved from absolute alcohol mixed with hydrate of potash, is much too large to be derived from the water in the hydrate of potash. Even when a small quantity of potassium is dissolved in alcohol of sp. gr. 0·7918 at 18·9° (whereby 1 At. hydrogen is expelled from the alcohol, and the compound $C^4H^5KO^2$ formed), such that the quantity of potassium dissolved in the alcohol shall, when reckoned as potash, amount to $\frac{1}{200}$ of the alcohol, this solution, when acted upon by 72 pairs of 4-inch plates, gives off 0·8 cub. in. of gas in 65 minutes; if the quantity of potash is equal to $\frac{1}{133}$ of the alcohol, the gas evolved in the same time amounts to 0·99 cub. in. The formation of gas, however, ceases entirely after the action has gone on for an hour; but it may be several times renewed by adding a fresh portion of potassium, and renewing the charge of the battery. Resin is also formed at the positive pole when potassium is dissolved in the alcohol. This experiment with potassium shows in the most convincing manner that alcohol, when subjected to the action of the electric current, is capable of evolving hydrogen from its own substance. (Connell.)

If the same electric current be passed through two voltameters (*App.* 29), the one containing water acidulated with sulphuric acid, the other absolute alcohol, whose conducting power [decomposibility,] has been increased by the addition of a small quantity of potash, boracic acid, iodide of potassium, chloride of calcium, or nitrate of lime, as much or nearly as much hydrogen is given off in a given time at the negative pole in the alcohol as in the acidulated water; *e. g.* 30 : 35; 32 : 34. (Connell.)

The chlorides and iodides of the alkali-metals are much less quickly decomposed in their solutions in absolute alcohol, than in their aqueous solutions, and yield at the negative pole, hydrogen gas and alkali [or potassium-alcohol, $C^4H^5KO^2$?], and at the positive pole, chlorine or iodine, which mix with the liquid there present (the iodine producing a brown colour), and produce a further action. — When the alcohol contains chloride of calcium (or nitrate of lime), the negative pole becomes covered with lime, which, being a non-conductor, stops the current. In an alcoholic solution of chloride of magnesium, magnesia is deposited in the form of a transparent crystalline layer, resembling native hydrate of magnesia. (Connell.) [Are not these deposits more probably $C^4H^5CaO^2$ and $C^4H^5MgO^2$?]. — When a solution 1 pt. iodide of potassium in 40 pts. absolute alcohol is placed in a cup connected with the negative pole of the battery, and also by means of two bundles of asbestus with two cups containing water, in the last of which the positive pole is immersed, gas is evolved at both poles; the liquid in the first cup acquires an alkaline, the other two an acid reaction, and the last becomes brown from separation of iodine, which by the secondary action of the oxygen there evolved, is subsequently converted into iodic acid. (Connell.) [The potassium and the hydrogen of the water move towards the negative pole; the iodine and the oxygen of the water towards the positive pole; the potassium at the negative pole decomposes the alcohol into hydrogen and $C^4H^5KO^2$; the oxygen of the water is evolved at the positive pole; the iodine, at the boundary between the first and second cup, takes up hydrogen from the water, the oxygen of which then goes towards the positive pole, while, at the same time, hydriodic acid is formed in the middle cup, and travelling further towards the positive pole, likewise makes its appearance in the positive cup; lastly, iodine combined with hydrogen arrives at the positive pole, is there separated, and partly converted into iodic acid by the oxygen there also evolved.] — Connell describes also a number of similar experiments with alcoholic iodide of potassium, hydriodic acid, and chloride of calcium, by which he endeavours to show that, in all cases, only the water is *directly* decomposed, viz., the water in the first cup, which he supposes to exist ready formed in the absolute alcohol. The solution of nitrate of lime in absolute alcohol yields hydrogen gas and lime [or $C^4H^5CaO^2$?] at the negative pole, and nitric acid, but no gas at the positive pole; the solution of nitrate of zinc in absolute alcohol yields a smaller quantity of hydrogen gas at the negative pole, together with zinc and zinc-oxide, [or $C^4H^5ZnO^2$?] (Connell.)

Since ether is not decomposed by the electric current, whereas the most anhydrous alcohol that can be obtained is probably decomposed thereby, Connell concludes that alcohol contains water ready formed, and is in fact a hydrate of ether; that the oxygen evolved from this water is not set free at the positive pole, but exerts a decomposing action on the alcohol there situated, the result of which is the formation of a resin.

But it is also possible that alcohol, in which there is no necessity for supposing the existence of water ready formed, may be resolved into hydrogen at the negative pole, and a dehydrogenated alcohol, probably aldehyde, (which view is corroborated by the experiments of Lüdersdorff) at the positive pole; this body may, in presence of water, be converted by the oxygen evolved therefrom into acetic acid, and in presence of potash, into aldehyde-resin.

A solution of shellac in absolute alcohol is decomposed by the electric current with even greater difficulty than pure absolute alcohol. (Hisinger & Berzelius.)

3. *Combustion.* Alcohol set on fire by the electric spark or by a flaming body burns in the air with a dull blue flame, and is converted into carbonic acid and water. Even if the supply of air be limited, the alcohol does not readily deposit soot; but absolute alcohol deposits it more readily than ordinary spirit. (Saussure.) The water produced by the combustion amounts to more than the alcohol burnt, a fact observed by the older chemists; for 46 pts. of alcohol contain 6 pts. hydrogen, which produce 54 water. In the condensed water Saussure found traces of ammonia, acetic acid, potash, and lime. The potash and lime must have proceeded from accidental impurities; the acetic acid probably from imperfect combustion of the alcohol; the ammonia perhaps from the nitrogen of the air combining with a portion of the hydrogen in the alcohol.

In oxygen gas the combustion is attended with very great evolution of heat. Hence its application first by Marcet, (*Ann. Phil.* 2, 99; also *Schw.* 11, 45) and afterwards by Stromeyer (*Schw.* 10, 270) to produce an extremely high temperature, by feeding an alcohol flame with a current of oxygen gas. (*Marcet's Blowpipe.*) — Alcohol vapour diffused through heated air or oxygen gas explodes on the approach of a flaming body; if the air or oxygen is saturated with the vapour, the mixture likewise explodes when an electric spark is passed through it. — Oxygen gas, saturated with alcohol-vapour at 21°, may still be exploded by the electric spark, if an excess of alcohol or $\frac{1}{5}$ vol. hydrogen gas is added to it. (Saussure.)

Imperfect Combustion. When alcohol or its vapour comes in contact with air, and with platinum and certain other metals, some of which act at ordinary, some at higher temperatures, the action being in all cases more powerful as the surface exposed is larger, an imperfect oxidation of the alcohol is produced at this surface, whereby the metals are generally heated to redness, and the alcohol is converted, not only into carbonic acid and water, but likewise into aldehyde, acetal, acetic acid, formic acid, acetic ether, and empyreumatic oil.

When E. Davy's *Platinum-black* (vi. 278, *c, a*) is shaken on paper moistened with alcohol, it makes a hissing noise and becomes red-hot, and if it does not set fire to the alcohol, continues to glow, and produce acetic acid as long as there is any alcohol left. (Edm. Davy, *Schw.* 31, 340.) — If the platinum-black be first moistened with a small quantity of water, or immediately covered completely with alcohol, the ignition and consequently the more complete combustion of the alcohol is prevented, and the alcohol is entirely converted, with evolution of heat, into acetic acid. The platinum-black remains unaltered in this action, and may be repeatedly to convert fresh quantities of alcohol into acetic acid. bereiner, *Schw.* 33, 414; also *Gilb.* 72, 194.)

The platinum-black is charged with oxygen from the air, and as it gives this oxygen to the alcohol, continually takes up fresh portions from the air. (Compare Delarive's theory of the action of platinum, II. 56). 4 at. oxygen combine with the elements of 1 at. alcohol, forming 1 at. acetic acid and 2 at. water.

$$C^4H^6O^2 + O^4 = C^4H^4O^4 + 2HO.$$

The formation of acetic acid appears to be preceded by that of aldehyde. The platinum-black becomes heated when thoroughly moistened with alcohol or with liquids containing alcohol, sets free a large quantity of gas, probably consisting of nitrogen from the absorbed air [?], and acquires a kind of fermenting motion, the gas-bubbles raising up the pasty mass, and bursting upon its surface, and continuing to escape till the alcohol is completely acidified. Acetic acid does not produce these phenomena unless it contains alcohol. (W. Döbereiner, *Schw.* 63, 477.)

Döbereiner's Vinegar-lamp. To the mouth of a bottle filled with absolute alcohol is adapted a glass funnel, in which are placed from 20 to 30 grains of slightly moistened platinum-black, to which the alcohol is brought from the bottle by a simple cotton-wick. The bottle is placed upon a dish, on which a bell-jar is inverted in such a manner as to admit of a certain circulation of air. Vapour of very strong and pure acetic acid is then evolved, condenses on the sides of the jar, and collects in the dish. As the platinum-black retains its power, it may be used to prepare any required quantity of acetic acid, even on the large scale (*vid. Acetic acid*). (Döbereiner, *Schw.* 47, 120; *Kastn. Arch.* 9, 342.)

Platinum-black affords therefore an excellent means of discovering the presence of small quantities of alcohol in the air or in watery liquids. If 4 grains of platinum-black, contained in a small basin, be introduced into 4 cubic inches of air, in which 1 grain of alcohol has evaporated, the sides of the vessel become covered in a few minutes with the acetic acid produced by oxidation of the alcohol. When weighed quantities of wine or beer are placed in connection with a graduated bell-jar filled with oxygen and containing platinum-black, as long as oxygen gas continues to be absorbed, the quantity of oxygen thus absorbed gives the quantity of alcohol contained in the liquid, inasmuch as 46 pts. of alcohol take up 32 of oxygen. (Döbereiner, *Schw.* 54, 416.)

Even if the greater part of the alcohol is converted into acetic acid by the slow combustion induced by platinum-black, there are still several other products formed.

If the combustion takes place in a space containing aqueous potash, the liquid becomes yellow in consequence of the formation of a resin. (Liebig, *Pogg.* 17, 105 to 106. — *Mag. Pharm.* 34, 55.)

If the supply of air be deficient, aldehyde is formed; and this, by the further action of the platinum-black and of oxygen gas, is completely converted into acetic acid, unless it be absorbed by caustic potash, in which case it is converted into a yellow resin [resin of aldehyde]. (Döbereiner, *Schw.* 63, 223.)

If a number of watch-glasses containing moist platinum-black, be placed above a dish containing alcohol, and a bell-jar open at the top be inverted over them, the alcohol turns sour in a few weeks, and is found to contain acetic acid, aldehyde, acetal and acetic ether. For, by neutralizing with chalk, saturating with chloride of calcium, and distillation, a liquid is obtained, whose boiling point rises, when it is heated, from 14° to 94°. If the half of this liquid be distilled off, the distillate yields with

ammoniacal gas, crystals of aldehyde-ammonia, and the residual half contains acetal, (which passes over at 94°,) and a small quantity of acetic ether. (Liebig, *Ann. Pharm.* 14, 138 and 155.)

If the vapour of alcohol is in excess, acetic ether is likewise produced. (Schweigger-Seidel, *Schw.* 63, 150.)

Connell (*N. Ed. Phil. J.* 14, 241), supposes that formic acid is likewise produced.

Remarkable also is the aromatic odour, like that of Borsdorf apples or very old wine, which is produced in this formation of acetic acid; the same was also once observed by Böttger on moistening sulphide of platinum with alcohol.

Other kinds of platinum-black and substances allied thereto, act in a manner precisely similar to E. Davy's platinum-black.

Platinum-black, 1, *a* (VI. 277) obtained from the alloy of zinc and platinum, sets fire to alcohol vapour mixed with air; when moistened with alcohol, it becomes red-hot, and exhales osmic as well as acetic acid; when mixed to a pasty consistence with a larger quantity of alcohol, and spread out in the air, it gives off acetic acid without becoming red-hot. (W. Döbereiner, *Pogg.* 37, 548, and *Ann. Pharm.* 17, 67.) — Berzelius's platinum-black, 1, *c*, previously freed from hydrochloric acid by potash, sets fire to alcohol vapour; and when immersed in it after being moistened with water, produces acetic acid, as also does Berzelius's platinum-black, 1, *d*. (W. Döbereiner, *Pogg.* 36, 308.)

Platinum-black, No. 2, moistened with alcohol, neither becomes red-hot nor produces acetic acid; nevertheless it exerts a decomposing action; for when enclosed in a vessel containing alcohol and air, it forms a gas having a suffocating odour [like that of aldehyde?], which is not carbonic acid. When enclosed in a vessel containing alcohol, oxygen, gas, and potash-ley, it causes the oxygen gas to be absorbed, whereupon the potash-ley assumes a yellow colour, deposits a flocculent precipitate, and emits an offensive soapy smell, which increases without any evolution of carbonic acid, on the addition of hydrochloric acid. (Liebig, *Pogg.* 17, 105.) — Platinum-black, No. 2, is denser, does not set fire to the alcohol so readily, and is, therefore, better adapted for the preparation of acetic acid. (Fr. Döbereiner, *Ann. Pharm.* 14, 259.)

Platinum-black, No. 3 (the so-called *oxidized sulphide of platinum*), does not become incandescent in contact with alcohol, but at most becomes heated, giving rise to the formation of acetic acid, and retains its activity unimpaired, even by long use. After being exposed for some time to the air, and well charged with oxygen, it converts alcohol into acetic acid, even out of contact of air. (W. Döbereiner, *Schw.* 38, 321; also *Gilb.* 74, 269, and *J. pr. Chem.* 4, 114.) — *Monosulphide of platinum* (but not the bisulphide,) moistened with alcohol, also converts it slowly into acetic acid. (Böttger, *J. pr. Chem.* 3, 270.)

Platinum-black, 4, *a* (VI. 278), obtained by means of formic acid, acts the most violently of all; sets fire to alcohol instantly; becomes red-hot even in the vapour of very weak alcohol; and when moistened with water, and introduced into air mixed with alcohol vapour, soon becomes so hot that it dries up, and then rises to redness. (W. Döbereiner, *Ann. Pharm.* 14, 10, and *J. pr. Chem.* 1, 269.)

Liebig's platinum-black, 4, *c*, γ, becomes red-hot when immersed in air containing alcohol-vapour, or when alcohol is dropped upon it; in the latter case it is only the part not wetted that glows; consequently if the *platinum* be wholly saturated with alcohol, it does not glow at all, but

nevertheless continues to form acetic acid. After it has been several times ignited in alcohol-vapour, it becomes welded together and loses its activity. (Liebig, *Pogg.* 17, 101.) — Platinum-black, 4, *d*, prepared with sugar (vi. 279) is, equally with (2), the best adapted for the preparation of acetic acid. (W. Döbereiner, *J. pr. Chem.* 1, 369.)

Iridium-black (VI. 370) acts similarly to platinum-black. (W. Döbereiner, *Schw.* 63, 477.)

Spongy platinum acts like platinum-black, but less strongly.— Moderately heated spongy platinum becomes red-hot when immersed in air loaded with alcohol vapour. (W. Döbereiner, *Schw.* 34, 91; Dana, *Sill. Am. J.* 8, 198; also *Schw.* 43, 380.) — Spongy platinum prepared by gently heating platinum sal-ammoniac, if heated to 100°, and then sprinkled with alcohol, or introduced into air containing alcohol, instantly becomes red-hot, and forms acetic acid. (Liebig, *Pogg.* 17, 105, and 114.) Platinum-balls prepared with meerschaum, (II. 49,) become red-hot in air containing alcohol, provided they have not absorbed water from the air. (W. Döbereiner, *J. pr. Chem.* 17, 158. — If a piece of spongy platinum be fastened by means of a fine platinum wire over the cotton wick of a spirit-lamp, the alcohol set on fire, and then blown out, the spongy platinum continues to glow; and this glow-lamp produces nothing but carbonic acid and water, no acetic or any similar acid. (Turner, *Edinb. Phil. J.* 12, 218.)

When alcohol of sp. gr. 0·793 is burnt in Böttger's glow-lamp, a liquid of sp. gr. 0·984 condenses in the head. This liquid is transparent and colourless, neutral to colours, has a not unpleasant odour resembling that of weak spirit, does not turn brown when boiled for a long time with oil of vitriol, does not precipitate nitrate of silver or chloride of gold, or dissolve mercuric oxide at a boiling heat; it is in fact nothing but water, containing a very small quantity of alcohol, which may, when separated by carbonate of potash, form a layer of inconsiderable thickness. (Böttger, *N. Br. Arch.* 13, 266; also *J. pr. Chem.* 10, 61 and 12, 334.)

It appears then that red-hot spongy platinum induces complete combustion of alcohol; but cold spongy platinum, which by itself exerts no action on a mixture of air and alcohol vapour, behaves in a totally different manner when moistened at the same time with alcohol and with a strong solution of potash or soda. It then becomes heated, often to redness, and converts the alcohol into aldehyde, resin of aldehyde, acetic acid, and polyosmone. (W. Döbereiner, *Ann. Pharm.* 53, 145.) [What is polyosmone ?]

Slow combustion of alcohol vapour mixed with air, likewise takes place at the surface of *metallic wires* and *laminæ*.

Fine platinum foil (II. 26, 6), strongly heated in a vessel containing air, and held over slightly heated alcohol, is brought into a state of continuous glow; so likewise is a spiral of platinum wire. (H. Davy, *Gilb.* 57, 246.) Metallic wires are generally made to act upon alcohol vapour in the glow-lamp. (II. 26, 5.) Platinum wire $\frac{1}{70}$ of an inch thick acts best; silver and nickel wires less readily; steel-wire still less (*e. g.* harpsichord wires, No. 8; they become oxidized and corroded in 9 hours, and then cease to glow); brass and copper wires produce scarcely any action. (Chladni, *Gilb.* 61, 346; 75, 98; Karmarsch, *Gilb.* 75, 83; Pleischl, *Schw.* 39, 355.)

In confined air the *ignition* of the platinum spiral of the glow-lamp continues till the proportion of oxygen in the air is reduced to 14¼ per

cent., by which time 4 per cent. of carbonic acid (but no carbonic oxide,) have been produced in it. But even when the spiral is no longer in a state of visible glow, it still continues to act for a certain time, (and, consequently, glows again when the air is admitted); the air which remains after the action is completely terminated, contains 8 p. c. oxygen and 8 p. c. carbonic acid gas. (Dalton, *Ann. Phil.* 12, 245; also *Gilb.* 61, 340.)

The combustion of alcohol in the glow-lamp produces scarcely anything but carbonic acid and water; nevertheless the peculiar odour, slightly resembling that of the so-called lampic acid produced in the slow combustion of ether, though not nearly so unpleasant, betrays the presence of other products.

If the glow lamp be provided with a cup, water condenses therein containing small quantities of alcohol, acetic acid, acetone, and empyreumatic oil. (A. Vogel. *Gilb.* 61, 344.) — The more brightly the platinum-spiral glows, the more completely is the alcohol burnt to carbonic acid and water; if it glows but feebly, aldehyde, acetic acid, and formic acid are also produced (the last may be detected by forming crystallized formiate of lead from it; if the wire is very thin, and the glow scarcely visible, and the supply of air likewise limited, aldehyde is formed without the two acids. Perhaps also acetic and formic ether are sometimes produced. (Martens, *N. Br. Arch.* 20, 181; abstr. *J. pr. Chem.* 18, 372.) Leroy (*J. Chim. méd.* 13, 583) states that he obtained a peculiar oily acid of sp. gr. 1·1315 by burning alcohol with a platinum spiral.

The oxides of the heavy metals, the earths, and *charcoal,* are likewise capable of exhibiting a continuous glow, when in contact with alcohol and air.

When sand contained in a dish is moistened with absolute alcohol, and covered with previously heated nickel powder, oxide of nickel, cobalt powder, cobaltoso-cobaltic oxide, uranoso-uranic oxide, stannic oxide (these six bodies being obtained by igniting the corresponding oxalates in an open or a covered crucible), or finely pulverized peroxide of manganese, these substances become heated to redness, and continue to glow as long as alcohol vapour rises. By this action, the nickel is converted into protoxide, and the peroxide of manganese into red-brown manganoso-manganic oxide (W. Döbereiner, *J. pr. Chem.* 1, 452.)

When the asbestus wick of a spirit-lamp is strewed with pulverized chromic acid, it sets fire to alcohol, and on blowing out the flame, the reduced chromic oxide forms a glow-lamp. (Böttger.)

Spirals of iron, copper, and brass, are not capable of forming a lamp without flame, till they have become oxidized on the surface, and they act the more strongly in proportion as the oxidation has been more complete [*compare* however Chladni, p. 209]. A spiral of iron wire almost wholly converted into oxide acts with nearly as much power as a platinum spiral (Böttger, *Ann. Pharm.* 57, 137). — If a flat piece of asbestus be finely frayed out at one end, by bending it backwards and forwards; the end sprinkled with peroxide of manganese, uranoso-uranic oxide, cadmic oxide, stannic oxide, ferric oxide, or nickel oxide; then held in the upper part of a flame of 80 p. c. alcohol; the flame carefully blown out; and the end of the asbestus lightly placed on the wick of a spirit-lamp, so that the two may just touch one another in a few points,—the oxide is brought into a state of vivid ignition, which lasts as long as the alcohol continues to evaporate. This experiment succeeds also with finely divided silver (genuine silver-bronze), and with finely divided gold

(precipitated by green vitriol), but not with finely divided iron (reduced from the oxide by hydrogen), or with finely divided copper (genuine copper bronze), unless these metals have been previously oxidized by heating them for some time. (R. Böttger, *Ann. Pharm.* 60, 117.)

Magnesia thrown in the red-hot state on paper moistened with alcohol, sometimes continues to glow, giving off at the same time a strong odour of lampic acid. (Venghaus, *Ann. Pharm.* 8, 70.)

Alcohol diluted with water, exhibits, when exposed under certain circumstances to the air, a combustion attended with but slight evolution of heat, and is ultimately converted into acetic acid. This formation of acid takes place with peculiar facility in presence of certain other organic substances which absorb the oxygen of the air, and appear to induce the alcohol likewise to enter into the state of oxidation (vid. *Acetous Fermentation.*) — But a mixture of a very small quantity of alcohol with a very large quantity of water contained in a loosely covered vessel, is converted into weak acetic acid, even without the addition of any other substance. The same change takes place in aromatic distilled waters, if they contain alcohol (Warington, *Phil. Mag. J.* 26, 574). In all these cases of the formation of acetic acid, the equation is:

$$C^4H^6O^2 + O^4 = C^4H^4O^4 + 2HO.$$

4. *Chlorine gas* is rapidly absorbed by alcohol, imparting to it a yellow colour, and causing a considerable rise of temperature, which, if the liquid be exposed to light, may even rise to inflammation; at the same time, it rapidly abstracts a continually increasing quantity of hydrogen, which is partly replaced by chlorine, thereby producing hydrochloric acid, aldehyde, acetal, acetic acid, acetic ether, chloride of ethyl, heavy hydrochloric ether, and finally chloral.

In this reaction, several series of decompositions appear to take place at the same time: *a.* Formation of aldehyde and then of chloral:

$$C^4H^6O^2 + 2Cl = C^4H^4O^2 + 2HCl;$$

then:

$$C^4H^4O^2 + 6Cl = C^4Cl^3HO^2 + 3HCl.$$

b. The hydrochloric acid formed in the process *a* acts upon another portion of the alcohol, and forms hydrochloric ether:

$$C^4H^6O^2 + HCl = C^4H^5Cl + 2HO;$$

the water thereby produced unites in part at least with the chloral, converting it into hydrate of chloral, whence even absolute alcohol always yields at the end of the action, not anhydrous, but hydrated chloral. The chloride of ethyl may, by the action of light and heat, be converted into other substitution-products, viz. $C^4H^4Cl^2$, $C^4H^3Cl^3$, and ultimately into C^4Cl^6, the last of which was, in fact, found in small quantity by Regnault (*Ann. Chim. Phys.* 71, 420) in the chloral formed towards the end of the process; it appears, however, to escape for the most part immediately after its formation, together with the hydrochloric acid gas which is abundantly evolved at the same time. — *c.* The acetal, which, according to Stas, is formed in hydrated alcohol at the beginning of the process (probably according to the equation: $3C^4H^6O^2 + 2Cl = C^{12}H^{14}O^4 + 2HO + 2HCl$) is perhaps subsequently converted into acetic acid:

$$C^{12}H^{14}O^4 + 8HO + 10Cl = 3C^4H^4O^4 + 10HCl.$$

d. Moreover, it is possible that acetic acid may be formed if the alcohol was originally hydrated, or has become so by process *b*:

$$C^4H^6O^2 + 2HO + 4Cl = C^4H^4O^4 + 4HCl,$$

and the acetic ether may be formed partly by the union of the acetic acid thus produced with another portion of alcohol, partly by direct action, as represented by the following equation:

$$2C^4H^6O^2 + 4Cl = C^8H^8O^4 + 4HCl.$$

As long, however, as the composition of heavy hydrochloric ether remains unknown, so long will it be impossible to give a complete account of the various modes of decomposition of alcohol by chlorine.

When chlorine gas is passed through alcohol in sunshine, flame is produced, as soon as the alcohol is partially saturated with chlorine (and thereby heated), so that every bubble of chlorine as it rises, produces a purple-red flame, shakes the apparatus, makes a slight detonation, forms white fumes, and deposits soot in the alcohol. (A. Vogel, *Kastn. Arch.* 7, 344.) — Liebig also observed the yellowish red flame accompanying the chlorine bubbles as they rise, and the deposition of soot which takes place if absolute alcohol is used and not kept cool.

Chlorine forms with alcohol, acetic ether and heavy hydrochloric ether. (Scheele.) — It moreover produces water, acetic acid, and a sweet substance. (Berthollet.) — It produces neither acetic ether, nor a sweet substance, but water, hydrochloric acid, heavy hydrochloric ether, a substance rich in carbon, a small quantity of carbonic acid, and a trace of acetic acid. (Thénard, *Mém. de la Soc. d'Arcueil*, 1, 147; 2, 25.) — Pfaff (*Schw.* 55, 204,) obtained with alcohol of sp. gr. 0·828 a large quantity of acetic ether and heavy hydrochloric ether, and a small quantity of acetic acid.

When absolute alcohol is saturated with dry chlorine at a temperature near 0°, it takes up a volume of chlorine equal to the volume of ethylene gas which it may be supposed to contain; half of this chlorine, however, is converted into hydrochloric acid. In this reaction the alcohol divides into two layers. The *upper layer*, amounting to $\frac{2}{3}$ of the whole, is very acid and fuming, and often coloured greenish by excess of chlorine. When mixed with water, it deposits drops of an oil identical with the lower liquid. The *under layer* is oily, of sp. gr. 1·23, has a more pungent odour than the oil of olefiant gas, $C^4H^4Cl^2$, and tastes somewhat sharper than oil of peppermint, but otherwise very much like it. When passed through a porcelain tube at a dull red heat, it yields nearly the same products of decomposition. After exposure to the air for a few hours, it gives off hydrochloric acid fumes. If free from hydrochloric acid, it does not dissolve perceptibly in water, but is decolorized by it. It appears, therefore, to be identical with $C^4H^4Cl^2$. Half of the chlorine combines with C^4H^4 to form this oil; the other half with the remaining 2H to form hydrochloric acid. (Morin, *Ann. Chim. Phys.* 43, 235; also *Pogg.* 19, 61.) [What becomes of the 2O in the alcohol?]

Chlorine gas passed through absolute alcohol is converted into about an equal volume of hydrochloric acid gas; moreover (if the chlorine or the alcohol is not perfectly anhydrous) oily drops of heavy hydrochloric ether are deposited, and form a layer which constantly increases, and in a few days becomes nearly equal in depth to that of the alcohol used. Above this there floats a thin layer of a sour-smelling liquid; and at length, if the liquid be not heated, the absorption of chlorine ceases. If the two

liquids be now separated by a dividing funnel, the lower liquid emits the odour of chloride of ethyl or of aldehyde, and has a burning and slightly sour taste. By repeated agitation the volume is reduced to $\frac{1}{8}$, not by solution in water but by decomposition; for when the water is distilled, or when the acid which it contains is saturated with potash, the heavy layer does not again separate from it. The heavy layer heated with aqueous potash yields a dark brown mixture from which acids precipitate a yellow resin [aldehyde-resin]. Potash appears to decompose oxygenated ether [aldehyde], into the resin and acetic acid; the water which has been shaken up with the heavy layer does not yield acetic acid by distillation, but hydrochloric acid and a peculiar volatile substance having a penetrating odour and burning taste [aldehyde?]; but this distillate, when heated with carbonate of potash, loses its odour, becomes brown and turbid, and is afterwards found to contain acetate of potash. (Liebig, *Mag. Pharm.* 34, 53.)

Ordinary alcohol saturated with chlorine deposits, on the addition of water, a heavy oil insoluble in hydrochloric acid, but dissolved, and in fact decomposed by pure water, in which case it yields a solution of hydrochloric acid and acetic ether [not also aldehyde? *vid. sup.*] This oil is probably therefore hydrochlorate of acetic ether $=(C^4H^5O,C^4H^3O^3)+2HCl$. (Liebig, *Ann. Pharm.* 8, 19; also *Pogg.* 31, 339.)

If the passage of perfectly dry chlorine gas through absolute alcohol kept constantly cool be continued as long as any absorption takes place, a yellow or yellowish green liquid is obtained, consisting chiefly of heavy hydrochloric ether. (This compound being soluble in hydrochloric acid does not separate unless the alcohol contains water.) This liquid, when heated, often boils suddenly, gives off hydrochloric acid gas and vapour of chloride of ethyl, and, after the hydrochloric acid has been expelled by sufficient heating, again absorbs chlorine gas till it is supersaturated with hydrochloric acid, whereupon it again assumes a yellow or yellowish green colour. If the hydrochloric acid and the chloride of ethyl be now again driven out by heat, chlorine is again absorbed, and this action may be repeated till the whole residue consists of hydrate of chloral. The same result is obtained if, in the latter part of the process, the alcohol be kept constantly warm, and the hydrochloric acid thereby continually driven out. When the experiment is conducted in this manner, the only products obtained are hydrochloric acid, chloride of ethyl, and hydrate of chloral; but neither carbonic acid, acetic acid, nor acetic ether is formed. (Liebig, *Ann. Pharm.* 1, 191; also *Pogg.* 24, 252.)

The chlorine probably converts the alcohol first into acetic ether:

$$2C^4H^6O^2 + 4Cl = C^8H^8O^4 + 4HCl.$$

Afterwards this compound is converted by substitution into chloral:

$$C^8H^8O^4 + 12Cl = 2C^4Cl^3HO^2 + 6HCl.$$

It is not, however, necessary that one of these two actions should follow the other; they may both go on together; 6 grammes of alcohol introduced into 6 litres of dry chlorine gas absorb the chlorine with evolution of heat, and the liquid distilled over chalk yields acetic ether. When chlorine is passed through alcohol, and the hydrochloric acid as it forms, removed by lime, a larger quantity of acetic ether is produced. In a similar manner, acetic ether passes over in the preparation of heavy hydrochloric ether, and is found in the upper layer of the distillate; but it disappears in proportion as the heavy hydrochloric ether increases;

hence the formation of the acetic ether precedes that of the heavy hydrochloric ether. (Dumas, *Ann. Chim. Phys.* 56, 123; also *Pogg.* 31, 666.)

Chlorine gas acting upon anhydrous alcohol forms aldehyde at first; if water is present, acetic ether may also be produced. (Cloez, *N. Ann. Chim. Phys.* 17, 297.) [But water is always formed by the reaction *b* (p. 211)].

A mixture of 1 pt. of 80 p. c. alcohol and 2 pts. water yields when saturated with chlorine gas, no other product of decomposition than aldehyde and hydrochloric acid. (Liebig, *Ann. Pharm.* 14, 137.)

In presence of a fixed alkali, the chief products formed by the action of chlorine upon alcohol are chloroform and carbonic acid.

Chlorine gas passed into alcoholic potash forms chloroform. (Soubeiran.) — Alcohol mixed with a strong solution of chloride of lime becomes heated, emits an odour of chlorine, and yields chloroform when distilled, while the residue, which has an alkaline reaction, deposits carbonate of lime and a small quantity of quicklime; acetate of lime does not occur in it. (Soubeiran, *Ann. Chim. Phys.* 48, 131; also *J. Pharm.* 18, 1; abstr. *Schw.* 65, 104.) The equation given by Soubeiran for this decomposition is incorrect.

According to the following experiments, however, acetic acid may likewise be formed in this reaction, at least if the lime is not in excess:

According to Hayes (*Sill. Amer. J.* 22, 141; abst. *Schw.* 65, 361), when chlorine gas or chloride of lime acts upon alcohol at a temperature near 0°, two peculiar acids are formed, viz., *Chlorovinic* and *Chlorovinous* acids; the former of which, in combination with lime, forms rectangular tables united in radiated groups, the latter six-sided prisms, which are permanent in the air. Schädler (*Ann. Pharm.* 14, 38), by using chloride of lime, obtained needles united in radiated groups and permanent in the air, but found them to consist of the compound of acetate of lime with chloride of calcium, described by Fritzsche. [Chloracetic acid might also occur.]

Chloride of lime containing excess of chlorine does not yield chloroform with alcohol. But, when the lime is in excess, chloroform is produced, and, at the same time, formiate of lime is deposited in crystalline grains; no gas is evolved:

$$2C^4H^6O^2 + 8(CaO,ClO) = 8HO + 5CaCl + C^2HCl^3 + 3C^2HCaO^4.$$

These 3 At. formiate of lime then react further upon the hypochlorite of lime, forming chloride of calcium and carbonic acid, which is precipitated with the excess of lime. (Liebig, *Chim. org.* 1, 574.)

$$3C^2HCaO^4 + 3(CaO,ClO) + 3CaO = 6(CaO,CO^2) + 3CaCl + 3HO.$$

5. *Bromine* mixed with alcohol becomes strongly heated, producing hydrobromic acid, bromide of ethyl, heavy hydrobromic ether, bromal, solid bromide of carbon (C^2Br^2), formic acid, water, and a flocculent substance not yet examined. (Löwig.)

If 6 ounces of absolute alcohol be put into a flask connected by means of three bent tubes with three Woulfe's bottles, and the quantity of bromine (from 15 to 16 oz.) required for the complete decomposition of the alcohol allowed gradually to flow in, violent heat and ebullition are at first produced. If the boiling be kept up by heat from without, and bromine frequently added, the boiling point then rises from 40° or 50° to 100°, and white flocks being at first deposited, which after-

wards disappear; and if the liquid be boiled till only $\frac{1}{4}$ remains in the flask, the following products are obtained: *In the flask* there remains an oily liquid coloured reddish yellow by free bromine, having a strong odour of bromal, and exciting a copious flow of tears; it is heavier than water, and consists of water, bromal, heavy hydrobromic ether, hydrobromic acid, free bromine, and formic acid. Exposed to the air, it deposits crystals of hydrate of bromal, while the heavy hydrobromic ether remains liquid. When kept for two days it separates into two layers, which contain the same products, but in different proportions. Small quantities of water separate heavy hydrobromic ether in the form of a yellowish oil (which dissolves in a larger quantity of water), taking up formic acid and bromal, which latter may be dissolved out by ether; the water set free therefrom reduces the metal from nitrate of mercury when heated with it; it therefore contains formic acid, perhaps produced from the bromal, *e. g.*, by the action of the alkali. — If the liquid which remains in the flask be immediately shaken up with ether, the lower stratum will be found to consist of aqueous hydrobromic acid and formic acid, and the upper of bromal and heavy hydrobromic ether dissolved in ether. If the ether be allowed to evaporate from this liquid and the residue be mixed with oil of vitriol, the mixture becomes heated, blackens, gives off hydrobromic acid gas, and separates into two layers; the lower, which is no longer decomposible by oil of vitriol, consisting of bromal — mixed, however, to judge from the sweetish odour, with bromide of carbon — while the upper, which is a fuming liquid, consists of hydrobromic acid mixed with oil of vitriol. If the residue, left after the evaporation of the ether, be treated with a small quantity of water instead of oil of vitriol, no crystals of hydrate of bromal are deposited, so long as the vessel is kept closed; to enable the heavy hydrobromic ether to evaporate, the liquid must be exposed to the air. Heavy hydrobromic ether is formed when perfectly anhydrous alcohol is dropped into boiling bromine. — In the *first Woulfe's bottle*, which was empty at the beginning of the operation, two layers are formed; the lower, which is coloured red by free bromine, deposits, after a few days, solid bromide of carbon, C^2Br^2, in the form of a white mass, and consists moreover of bromide of ethyl. The upper colourless layer contains a very large quantity of bromal; if the greater part of this be removed by ether, there remains an acid liquid, which, after being neutralized with soda, yields a distillate of bromoform (formed by the action of the soda on the bromal still present), and formiate of soda together with bromide of sodium remains in the retort. — In the *second bottle*, which originally contained water, nothing is found but aqueous hydrobromic acid; and in the *third bottle*, which originally contained caustic potash, nothing but bromide of potassium. No permanent gas is evolved in this operation, *i. e.*, no carbonic acid. (Löwig, *Ann. Pharm.* 3, 288.)

6. *Iodine* introduced into absolute alcohol dissolves at first as such, forming a dark brown solution; but afterwards forms hydriodic acid and iodide of ethyl, very slowly at ordinary temperatures, more quickly when heated.

Recently prepared tincture of iodine (1 pt. iodine in 10 pts. alcohol) yields a copious precipitate with water; but the same tincture, after being kept for four months, yields but a slight precipitate (the liquid above the precipitate being coloured very dark red by hydriodous acid),

and, after a year or eighteen months, a scarcely perceptible turbidity, when mixed with water. (Guibourt, *N. J. Pharm.* 10, 113.)

A concentrated solution of iodine in alcohol assumes a straw-yellow colour when chlorine gas is passed through it, and deposits a white substance which is permanent in the air and not perceptibly soluble in water. Oil of vitriol added to the straw-yellow liquid liberates vapours of iodine; ammonia throws down iodide of nitrogen, &c. (Inglis, *Phil. Mag. J.* 7, 422.)

Respecting the production of iodoform from alcohol, iodine and potash, *vid.* VII, 331—334.

If, to the dark brown solution of 1 pt. iodine (previously converted by chlorine into protochloride of iodine) in 5 pts. alcohol, alcoholic potash be added in small portions till it is slightly in excess, iodide of potassium is thrown down together with iodate of potash (the acid iodate at first, afterwards the neutral), and the decanted liquid, which has assumed a yellow colour, yields, on evaporation, crystals of iodoform. If potash be not present, no iodoform is produced, not even if the potash be replaced by lime, magnesia, or iron. (Serullas, *Ann. Chim. Phys.* 22, 172.)

7. *Phosphorus* appears to decompose alcohol only in the presence of other substances.

The solution of phosphorus in absolute alcohol remains unaltered in close vessels. (Zeise.) When a tin case, in which sticks of phosphorus had been soldered up together with alcohol, was opened, after a considerable time, an intolerable stench was emitted; the alcohol burst forcibly out at the joints, smelt disagreeably, was black, and reddened litmus strongly; the sticks of phosphorus were blackened on the surface. (Strauss, *Jahrb. prakt. Pharm.* 8, 16£.)

Finely divided phosphorus immersed in a concentrated solution of hydrate of potash in absolute alcohol contained in a close vessel, forms in a few hours, a turbid, chocolate-coloured liquid. If this be quickly filtered, a large quantity of brown mud remains on the filter. The clear dark brown filtrate A soon becomes turbid, and deposits a similar mud, which indeed is continually reproduced, even after repeated filtering, till the liquid becomes decolorized, in which state it appears to contain nothing but hypophosphite of potash. — If water be poured upon the brown deposit on the filter, immediately after the alcoholic liquid has run off, it dissolves with the exception of a trace of brown-black matter, forming a brown solution, from which hydrochloric acid throws down a great number of large yellow flakes of *Phosoxycarbyl.* — But if the brown deposit be left for an hour after the alcohol has been poured off — in which case it assumes a greyish brown colour — and then treated with alcohol, it no longer dissolves, but if water be repeatedly poured upon it, becomes continually lighter in colour, and at last greyish yellow; and if then treated with hydrochloric acid, it is converted into yellow phosoxycarbyl. — This phosoxycarbyl becomes reddish yellow when dried in the air, and bark brown-red in vacuo over oil of vitriol. When subjected to dry distillation, it first gives off a non-inflammable white vapour which condenses to an almost pulverulent substance, then a small quantity of phosphorus, and leaves a considerable quantity of carbonaceous matter. Phosoxycarbyl is not soluble in alcohol. (Zeise.)

If carbonic acid gas be passed through the brown filtrate A immediately after filtration, a brownish grey substance of slightly muddy consistence separates in large quantity; and when this is thrown upon a

filter a colourless liquid runs off, apparently containing hypophosphite of potash, inasmuch as, when evaporated to dryness and heated, it gives off spontaneously inflammable phosphuretted hydrogen gas. The precipitate collected on the filter assumes, when washed successively with alcohol and water, first a greyish yellow, then a pure yellow colour, in which state it appears to consist also of phosoxycarbyl. (Zeise.)

When phosphorus is placed with alcoholic potash in a close vessel for 24 hours instead, of only a few, and then filtered, the substance left on the filter is much smaller in quantity, exhibits a greyish black colour, and contains but little that is soluble in water. — When an excess of phosphorus is boiled with alcoholic potash, the brown substance is not produced, but a colourless liquid is immediately formed, which appears to contain hypophosphite of potash [such at least is the case according to H. Rose (III. 27.)] (Zeise, *J. pr. Chem.* 26, 85; also *Ann. Pharm.* 41, 35.)

8. *Nitric oxide gas* strongly charged with alcohol-vapour is not altered by passing over spongy platinum at ordinary temperatures, but at a red heat deposits carbon, and is resolved into carbonate and hydrocyanate of ammonia. (Kuhlmann, *Ann. Pharm.* 29, 284.) — Sulphate of nitric oxide introduced into alcohol immediately converts it into nitrous ether, without evolution of nitrogen. (H. Rose, *Pogg.* 74, 606.) — The solution of sulphate of nitric oxide in alcohol (II. 447,) gives off nitric oxide and nitrous ether when strongly heated, assuming at first a violet colour, and finally leaving a yellow residue which does not contain nitric acid. (Döbereiner, *Schw.* 8, 253.)

9. *Nitric acid* decomposes alcohol with great evolution of heat and brisk ebullition, a mixture of various elastic fluids — the *ethereal nitrous gas* of the older chemists — being evolved, and an acid liquid remaining behind. The gaseous mixture consists of nitrogen, nitrous oxide (a large quantity), nitric oxide, hyponitric acid vapour, aqueous vapour, carbonic acid gas, the vapours of hydrocyanic acid, aldehyde, acetic acid, acetic ether, formic acid, formic ether, and a large quantity of nitrous ether,—and when passed into a well cooled receiver, deposits the greater part of these vapours in the liquid form. The liquid, often small in quantity, which remains when the effervescence has ceased, contains nitric acid, undecomposed alcohol, aldehyde, saccharic acid (artificial malic acid), oxalic acid, together with other substances not yet sufficiently examined.

The products obtained in this decomposition of alcohol are not exactly derived from the nitric acid as such, but rather from the nitrous acid resulting from the previous reduction of part of the nitric acid by the alcohol. Nitrous acid in contact with nitrate of urea is immediately resolved into water, nitrogen, and carbonic acid gas (VII, 367). If then nitrate of urea be added to a mixture of alcohol and moderately strong nitric acid, the nitrous acid is decomposed as fast as it forms, and before it has time to act upon the alcohol, so that the distillate consists wholly of nitric ether, water, and undecomposed alcohol. (Millon, *N. Ann. Chim. Phys.* 8, 232.)

Fuming nitric acid mixes with about twice its weight of strong alcohol, quietly at first, excepting that a slight percussion or detonation is heard now and then. But soon the mixture becomes hot; begins to give off bubbles; is thrown into a state of the most violent percussive ebullition; giving off large quantities of ethereal nitrous gas in streams

of a vapour which turns red in the air and falls down; and only a small quantity of an acid liquid is left in the vessel.

Moderately dilute nitric acid does not exert any remarkable action on an equal quantity of alcohol at ordinary temperatures; but on the application of a gentle heat, so violent an intumescence takes place, that to prevent frothing over, it is necessary to cool the vessel by pouring cold water upon it, whereby the effervescence is diminished but by no means stopped. (Thénard, *N. Gehl.* 4, 19.)

The constituents of the ethereal nitrous gas were all distinguished by Thénard, with the exception of hydrocyanic acid, aldehyde, formic acid and formic ether.

The vapour which is given off in the preparation of *Spiritus nitri dulcis* on the large scale, kills rabbits instantly, and exerts a poisonous action on man; a trace of hydrocyanic acid may be detected in it. (F. Simon, *Br. Arch.* 32, 373. — Gaultier de Chaubry (*J. Pharm.* 25, 764; also *J. pr. Chem.* 19, 317), and Dalpiaz (*N. J. Pharm.* 5, 239), afterwards established the presence of the hydrocyanic acid more decidedly. Gaultier de Claubry also found formic acid and formic ether in the vapours given off in the preparation of fulminating mercury, and Dalpiaz found a large quantity of formic acid in *Spiritus nitri dulcis.*

The distillate obtained with alcohol and nitric acid must contain oxygen-ether (aldehyde), inasmuch as it forms a resin with alcoholic potash. (Döbereiner, *Gilb.* 74, 414; *Pogg.* 24, 606.) — Duflos (*Schw.* 64, 468) likewise obtained aldehyde.— When 3 pts. of 80 p. c. alcohol are distilled with 2 pts. of nitric acid of sp. gr. 1·25, acetic acid and a large quantity of aldehyde pass over as well as nitrous ether. (Liebig, *Ann. Pharm.* 14, 137 and 154.)

If nitric acid, water, and alcohol be arranged in layers one above the other in a bottle, as in Black's method of preparing nitrous ether, and after they have acted upon one another for two days in the cold, the resulting very acid ethereal layer be decanted off, it will be found not to contain aldehyde. It is true that when distilled, it first yields nitrous ether and then a distillate which turns brown with potash, reduces silver, and therefore contains aldehyde; but this product is actually formed during the distillation by the acid still present. For, if the ethereal layer be neutralized with oxide of lead before distillation, no aldehyde passes over. Hence an elevated temperature is required for the formation of the aldehyde. — The acid liquid from which the ethereal layer has been decanted, contains a large quantity of acetic acid as well as nitric acid. (Golding Bird, *Phil. Mag. J.* 14, 324; also *J. Pharm.* 25, 571.)

Respecting the acid liquid which remains after the action of nitric acid upon alcohol, the following statements have been made, the discrepancies in which are probably due to the various proportions of acid and alcohol used, and to the different times during which the heating has been continued:

8 pts. of alcohol with 24 pts. nitric acid yield 1 pt. of oxalic acid. (Bergman.) — 14·7 pts. alcohol with 41 pts. of fuming nitric acid yield 1 pt. of oxalic acid. (Sage.)

The residue of the distillation of equal parts of alcohol and moderately strong nitric acid does not contain oxalic acid, but nitric acid, alcohol, a small quantity of acetic acid, and an indefinite substance which chars readily; when further heated, it gives off carbonic acid, nitric oxide, and nitrogen, and is converted into a viscid substance consisting of oxalic acid, and, perhaps, of a small quantity of artificial malic acid. (Thénard.)

In the first distillation of alcohol with nitric acid, a sweet residue is left; this residue distilled a second time with nitric acid becomes bitter, and if then again distilled with nitric acid, yields oxalic acid. (Donovan, *Ann. Chim. Phys.* 1, 294.)

5 pts. of alcohol distilled with 1 pt. of fuming nitric acid, yield, after the acid liquid has been evaporated in the air, a residue like gum arabic; but 5 pts. alcohol with 2 pts. fuming nitric acid yield crystallized oxalic acid. (Hermbstädt, *Kastn. Arch.* 22, 151.)

When 1 pt. of alcohol of 38° Bm. is heated with 3 pts. of commercial nitric acid, till it begins to boil up, and the mixture then removed from the fire, the acid residue, if supersaturated at the end of the reaction with caustic or carbonated ammonia, potash, or soda, assumes a fine red colour. A similar reaction is exhibited by the residue of a mixture of alcohol with $\frac{1}{8}$ pt. of fuming nitric acid, after the spontaneous ebullition has ceased. A red liquid of this nature slightly supersaturated with potash precipitates metallic silver from the nitrate, and forms, with neutral acetate of lead, a precipitate which appears to consist of saccharate of lead. (Rouchas, *J. Pharm.* 17, 116; also *N. Tr.* 24, 2, 187.)

The pale yellow residue which remains after the distillation of 1 pt. nitric acid with about 9 pts. alcohol of sp. gr. 0·85, smells of nitrous ether. When exactly neutralized with potash, it becomes yellowish brown and somewhat turbid; does not precipitate lime-salts, and is, therefore, free from oxalic acid; but throws down saccharate of lead from a solution of the acetate (the lead-salt does not melt or dissolve perceptibly in boiling water, and the acid ammonia-salt crystallizes in needles). The residue neutralized with potash does not turn dark brown under 70°; it has an offensive soapy smell. — If the residue after neutralization with potash be evaporated to a syrupy consistence, in which case nitrous fumes are given off in abundance, oxalic acid crystallizes out from the liquid. If it be fractionally distilled, nitrous ether passes over at first, and the residue exhibits but a small amount of oxalic acid; if the distillation be continued till the nitrous fumes begin to appear, a distillate rich in aldehyde passes over, and the residue contains a large quantity of oxalic acid; on continuing the distillation still further, the quantity of oxalic acid still increases, but the distillate contains but little aldehyde, and, consequently, assumes but a faint yellow colour when treated with potash. The distillate containing the larger quantity of aldehyde smells very pungent, excites tears, and tastes agreeably at first, but afterwards burning like pepper. It assumes an orange-yellow colour when treated with potash, becoming darker when heated, acquires a soapy smell, and if then treated with sulphuric acid, yields a yellow precipitate of aldehyde-resin. It likewise, when neutralized with ammonia, forms with nitrate of silver a white precipitate which reduces to silver when heated. Consequently, aldehyde has passed over in the distillate, and oxalic acid has been formed. (Golding Bird, *Phil. Mag. J.* 14, 324; also *J. Pharm.* 25, 571.)

If to the mixture of 1 pt. alcohol and 1 pt. fuming nitric acid, while yet in the state of violent ebullition, there be added 1 pt. of oil of vitriol, it bursts out into flame [this never succeeded within the Author's experience]; on mixing these three liquids in a retort, violent ebullition takes place, and nitrous ether passes over into the receiver, together with a greenish, pleasant-smelling oil which floats upon it. (Brugnatelli, *Schw. J.* 4, 250.)

Uranic nitrate dissolved in alcohol decomposes it when heated, and forms nitrous ether. (Bucholz, *A. Gehl.* 4, 153.) — Nitrate of nickel does

not dissolve in absolute alcohol, but causes an evolution of heat, assumes first a yellow and then a green colour, and emits an ethereal odour.— Mercuric nitrate and nitrate of silver heated with alcohol and excess of nitric acid, yield the above-mentioned products formed by nitric acid, and likewise a precipitate of fulminate of mercury or silver.

If to a mixture of equal parts of alcohol and nitric acid, a small quantity of iodine be added during the violent action, this action immediately ceases, nitrous oxide gas is slowly evolved, and a few oily drops are precipitated, probably consisting of iodal; if the iodine is in excess, the drops exhibit a green or red colour. — Bromine acts upon a mixture of alcohol and nitric acid, in a similar manner, excepting that it liberates nitric oxide instead of nitrous oxide. (Aimé, *Ann. Chim. Phys.* 64, 217; also *Ann. Pharm.* 23, 258; also *J. pr. Chem.* 12, 188.)

10. *Hypochlorous acid* converts alcohol in acetic acid and an oily liquid, without evolving chlorine or carbonic acid gas. (Balard.)

Alcohol, through which chloric oxide gas is passed, acquires a deep yellow colour, and a fruity odour mixed with that of chlorine. It loses the chlorine-odour in a few hours and turns sour, and if then subjected to fractional distillation, yields a yellow liquid, which has a scarcely perceptible acid reaction, an agreeable fruity odour, and perhaps consists of chlorous ether, C^4H^5O,ClO^3; in a few hours this liquid gives off chlorine, and is wholly converted into acetic ether. In the retort there remains a strongly acid liquid which smells of acetic acid. The same distillate is obtained when pieces of fused and solidified chlorate of potash are gradually added to a mixture of alcohol and oil of vitriol in a tubulated retort; each piece causes brisk effervescence and evolution of chlorine and chlorous ether; but acetic ether is evolved at the same time, and sometimes nothing else. (Soubeiran, *Ann. Chim. Phys.* 48, 152.) — Bercht observed long before (*Gilb.* 36, 103), that on distilling a gradually prepared mixture of 12 pts. alcohol, 2 pts. chlorate of potash, and 1 pt. oil of vitriol, acetic ether is given off. — If the oil of vitriol causes great rise of temperature, the mixture takes fire. On mixing 10 grains of chlorate of potash with 4 drams of alcohol, and then adding about 6 drams of oil of vitriol, blue fiery bubbles rise up and set fire to the mixture. (Accum.)

A few drops of *Chloric acid* poured upon alcohol cause it to take fire. (Langlois, *J. Chim. méd.* 16, 382.) — Concentrated chloric acid converts alcohol of 40° Bm. into very strong acetic acid, at the same time causing it to boil violently, and, if in small quantity, to take fire. If the chloric acid and alcohol are more dilute, and are mixed in a long glass tube, slight detonations are heard from time to time, and after each detonation, the yellow colour of the mixture disappears for awhile. (Serullas, *Ann. Chim. Phys.* 45, 203; also *Pogg.* 20, 591.) — When alcohol is gradually added to chloric acid in the proportion of 2 pts. alcohol to 15 chloric acid, a violent explosion which bursts the tube takes place, as soon as about 1 gramme of the alcohol has been added. (*J. Pharm.* 18, 385.)

When 1 vol. concentrated *Perchloric acid* is distilled with 2 vols. of 90 per cent. alcohol, alcohol passes over first; then as the boiling point rises, common ether makes its appearance in the distillate; afterwards white fumes arise, which yield a distillate smelling of oil of wine; and the residue turns black. The acid does not appear to be decomposed in this reaction, but yields more ether when distilled with a fresh quantity of alcohol. — No such compound as perchlorovinic acid (analogous to sul-

phovinic acid) is obtained by mixing alcohol with perchloric acid, even at high temperatures. (Weppen, *Ann. Pharm.* 29, 317.)

11. A mixture of 4 grms. of moderately strong *Bromic acid* and 4 grms. alcohol becomes coloured almost instantly, and rises to a state of brisk ebullition, giving off large quantities of bromine vapour and acetic ether (no carbonic acid); the residual yellow liquid contains acetic acid and a small quantity of hydrobromic acid, formed by the action of the liberated bromine on the excess of alcohol. If the bromic acid is in excess, the alcohol is wholly converted into acetic acid and acetic ether. (Serullas, *Ann. Chim. Phys.* 45, 203.)

12. When a solution of *Selenious acid* in alcohol is distilled, a small quantity of selenium is reduced, and a distillate is obtained which smells of common ether and nitrous ether, and from which chloride of calcium does not separate any ethereal liquid. A mixture of alcohol, selenious acid, and oil of vitriol yields a considerable quantity of reduced selenium, and a distillate having an intolerable odour. (Berzelius, *Ann. Chim. Phys.* 9, 180.)

13. Absolute alcohol, at ordinary temperatures, slowly absorbs the vapour of *anhydrous Sulphuric acid*, and yields crystals of sulphate of carbyl ($C^4H^4,4SO^3$), together with ethionic acid, isethionic acid, sulphovinic acid (which acids may be regarded as compounds of alcohol with anhydrous sulphuric acid), and hydrated sulphuric acid (Magnus, *Pogg.* 47, 509.) — On distilling a mixture of absolute alcohol and anhydrous sulphuric acid which has been made in such a manner as to avoid all rise of temperature, undecomposed alcohol passes over at first, provided that the sulphuric acid is not in excess; then common ether, which is always formed unless the sulphuric acid is in very great excess; then sulphurous acid and olefiant gas, and a colourless, strongly acid, viscid liquid, probably a compound of sulphuric acid with a hydrocarbon, which yields oil of wine when digested with water. (Kuhlmann.) — A mixture of 231·7 pts. (2 At.) absolute alcohol, and 100 pts. (1 At.) anhydrous sulphuric acid, begins to boil at 120°; gives off 131·85 pts. of undecomposed alcohol at 135°; and above 135°, yields ether, sulphurous acid, olefiant gas, and the viscid liquid. The ether produced in this reaction, and proceeding from 99·75 pts. of decomposed alcohol, amounts to 24 per cent. — 115·85 pts. (1 At.) alcohol and 100 pts. (1 At.) sulphuric acid give off between 120° and 130°, a certain quantity of alcohol without ebullition; then at 135°, at which temperature the mixture begins to boil, 21·23 pts. of alcohol containing ether; then between 140° and 175°, 23 pts. of pure ether; and, lastly, at 175°, sulphurous acid [and olefiant gas ?] and the viscid liquid. The 94·62 pts. of alcohol thus decomposed, yield 24·3 p. c. ether. — 86·88 pts. (3 At.) alcohol and 110 pts. (4 At.) sulphuric acid. The colourless viscid mixture boils completely at 140°, does not give off any undecomposed alcohol between 140° and 180°, but only ether (amounting to 44·25 per cent. of the alcohol), after which it yields sulphurous acid gas, and at 200, olefiant gas, together with the colourless, viscid liquid. — 77·23 pts. (2 At.) alcohol and 100 pts. (3 At.) sulphuric acid do not yield any alcohol, but between 140° and 160°, give off ether (amounting to 16·13 per cent. of the alcohol); then at 170°, sulphurous acid and olefiant gas; and at 180°, sulphurous acid gas, oil of wine, and water.— 57·92 pts. (1 At.) of alcohol and 100 pts. (3 At.) of sulphuric acid yield, between 120° and 140°, sulphurous acid; at 150°, the viscid liquid which

yields oil of wine when mixed with water; at 160°, sulphurous acid and olefiant gas; and at 180°, the viscid liquid, after which, at 200°, the residue swells up. — With 1 At. alcohol to 4 At. sulphuric acid the same result is obtained, excepting that anhydrous sulphuric acid likewise passes over, solidifying at 0°.

In examining the action of *Oil of Vitriol* on alcohol, there are three stages to be considered: *a. Formation of Sulphovinic acid; — b. Formation of Ether and Water; — c. Formation of Sulphurous acid, Olefiant gas, Oil of Wine, Carbonic acid, Acetic acid, Carbonaceous matter, &c.*

a. Formation of Sulphovinic acid.

Oil of vitriol mixes with alcohol, producing considerable evolution of heat, often sufficient to boil the alcohol, which still remains uncombined, and is then converted, together with the alcohol—provided the latter be not kept very cold—into sulphovinic and dilute sulphuric acid.

This formation of sulphovinic acid was discovered by Sertürner. The indication by which it may be known to have taken place is, that the mixture, when diluted with water and digested with excess of oxide of lead or carbonate of baryta or of lime, yields a smaller quantity of sulphate than that which is due to the oil of vitriol used,—and that the liquid filtered from this salt contains an easily soluble, crystalline salt, the sulphovinate. Since sulphuric acid, by conversion into sulphovinic acid, loses half its capacity of saturation, inasmuch as 1 At. $C^4H^6O^2,2SO^3$ saturates no greater quantity of base than 1 At. SO^3, the quantity of sulphovinic acid produced in the mixture may likewise be calculated from the quantity of base which the mixture can saturate after the action has taken place.

When 1 pt. of the most highly rectified spirit is rapidly mixed with 1 pt. oil of vitriol, the temperature of the mixture rises to 87°; and 1 pt. of the same spirit with 2 pts. sulphuric acid rises to 94°. The latter mixture is dark red, but becomes black in a few days, and emits a distinct odour of ether. (Fourcroy & Vauquelin, *Ann. Chim.* 23, 203.)

1 pt. of of alcohol of 40° Bm. cautiously mixed with 1, 2, 3, or 8 pts. of oil of vitriol, yields a colourless mixture, which, if 1 or 2 pts. of acid are used, smells distinctly of alcohol, while, with 3 pts. acid, the odour of alcohol is scarcely perceptible, and with 8 pts. acid, it vanishes altogether; but if the liquids be suddenly mixed, the heat evolved causes the mixture to turn brown, and if the quantity of oil of vitriol is twice or three times that of the alcohol, the odour of ether becomes perceptible. (Boullay, *J. Pharm.* 1, 109.)

100 pts. of alcohol rapidly mixed with 100 pts. of oil of vitriol, form a brown mixture; but if the oil of vitriol be dropped into the alcohol so slowly as not to cause any rise of temperature, a yellow mixture is obtained. 200 pts. of the first mixture diluted after 14 days with water, and mixed with acetate of lead, yield 90·32 pts. sulphate of lead; 200 pts. of the second mixture similarly treated, yield 109·08 pts. sulphate of lead. Hence, out of the 81·6 pts. of anhydrous sulphuric acid contained in the 100 pts. oil of vitriol, 23·8 pts. remain unaltered in the first experiment, and 28·7 in the second. (J. A. Buchner, *Repert.* 19, 198.)

If a mixture of equal parts of alcohol and oil of vitriol be distilled, till about half the ether which it is capable of yielding has passed over,

it will then be found to contain more sulphovinic acid than before the distillation. The residue left after all the ether is distilled over, still contains sulphovinic acid, but if it has been heated enough to convert it into a carbonaceous mass, it no longer contains that acid. (A. Vogel, *Gilb.* 63, 84.)

When equal parts of alcohol of sp. gr. 0·82 and oil of vitriol are mixed together, $\frac{3}{5}$ of the sulphuric acid are converted into sulphovinic. (Hennel.)

In a mixture of equal parts of 80 per cent. alcohol and oil of vitriol, $\frac{2}{3}$ of the sulphuric acid are thus converted. (Dulk, *Berl. Jahrb.* 1820, 382.)

If a basin containing 1 pt. of alcohol be placed near another containing oil of vitriol of sp. gr. 1·830, both being under a bell-jar not exhausted of air, the alcohol, as it evaporates, is quickly absorbed by the oil of vitriol, but the mixture does not become perceptibly warm; on saturating it with carbonate of baryta, half the sulphuric acid is found to be converted into sulphovinate, so that the quantity of baryta combined with the sulphuric acid is to that which is combined with the sulphovinic acid almost exactly as 2 : 1. Even when the alcohol is in great excess, only half of the sulphuric acid is converted into sulphovinic. The portion of sulphuric acid which remains unaltered must, after this change, contain 2 At. water :

$$C^4H^6O^2 + 4(HO,SO^3) = C^4H^6O^2,2SO^3 + 2(2HO,SO^3).$$

Hence sulphuric acid, after it has taken up 2 At. water, is no longer capable of forming sulphovinic acid. (Magnus, *Pogg.* 27, 274.)

When 1 pt. oil of vitriol of sp. gr. 1·840 is mixed with from $\frac{2}{3}$ to 1 pt. of absolute alcohol, in such a manner as not to make the mixture hot, $\frac{4}{5}$ of the sulphuric acid are converted into sulphovinic, so that, when this mixture of the two liquids in equal portions is diluted with water and mixed with chloride of barium, only from 21·7 to 22·8 per cent. of sulphate of baryta is precipitated. The more the sulphuric acid is diluted with water, the smaller is the quantity of it converted into sulphovinic acid; and the formation of this compound ceases altogether when the sulphuric acid is reduced by dilution to a sp. gr. of 1·63 ($= 3HO,SO^3$). Duflos (*Kastn. Arch.* 12, 167, 18, 371.)

When 1 At. (49 pts.) of oil of vitriol is added, slowly and with agitation, so that no heating may take place, to 1 At. (from 46 to 55 pts.) of absolute or of 85 per cent. alcohol surrounded with a mixture of ice and salt, a mixture is formed containing no sulphovinic acid, that acid not appearing in it even after several days, provided it be kept surrounded with melting ice. But at higher temperatures, even between $+10°$ and 15°, sulphovinic acid is gradually produced, so that after three or four days 77 per cent. of the sulphuric acid is converted into it. The same change takes place in a few hours between 30° and 35°, and in a few minutes if the mixture be immersed in boiling water; but strong sunshine has no effect upon it. If a large quantity of alcohol be poured into the oil of vitriol so that strong heating takes place, the formation of sulphovinic acid is completed in an instant. This quantity of sulphovinic acid is not increased by leaving the liquids together for a longer time. When the alcohol and sulphuric acid are mixed in equal parts, the quantity of sulphuric acid converted into sulphovinic never exceeds 77 pts. in 100. — When 2 At. absolute or 85 per cent. alcohol, are mixed with 1 At. oil of vitriol, the same phenomena are produced; but, in this case, the formation of the sulpho-

vinic acid may be prevented by cooling, even more easily than in the former; and on heating the mixture, the quantity of sulphuric acid converted into sulphovinic never exceeds 73 or 74 per cent. — When, on the other hand, 1 At. alcohol is mixed with 2 At. oil of vitriol, sulphovinic acid is formed, under all conditions, even at the lowest temperatures, and the proportion of sulphuric acid converted into sulphovinic is never less than 55 per cent. It makes no difference whether the alcohol be poured into the oil of vitriol, or the contrary; whether the mixture be cooled or not; whether it be left to stand for some time and then heated in boiling water—whereby it does not suffer any loss of weight (a proof that even the portion of alcohol not actually used for the formation of sulphovinic acid, has entered into some state of combination)—or not. (Millon, *N. Ann. Chim. Phys.* 19, 227; also *Comp. rend.* 23, 939.)

In a mixture of 1 pt. oil of vitriol and 1 pt. water mixed with 4 pts. of alcohol, no sulphovinic acid is produced; but if, from this mixture, 4 pts. consisting of water and alcohol be distilled, a residue will be left containing a large quantity of sulphovinic acid. Hence, as the proportion of water diminishes, the alcohol takes from the water a portion of the sulphuric acid. (Hennel.)

Since a mixture of equal parts of oil of vitriol and 85 per cent. alcohol, in which 2 At. sulphuric acid are mixed with 1·8 At. alcohol, does not boil below a temperature between 112° and 124°, all the alcohol in it must be in the combined state, although 2 At. sulphuric acid require only 1 At. alcohol to form sulphovinic acid. — A mixture of 9 pts. oil of vitriol and 5 pts. of 85 per cent. alcohol, in which 2 At. sulphuric acid are brought in contact with 1 At. alcohol and 3 At. water, contains all the alcohol in the form of sulphovinic acid; for dry chlorine passed through it does not form hydrochloric acid gas. — A mixture of 9 pts. oil of vitriol and 5 pts. of 85 p. c. alcohol, or — which comes to the same thing — of 98 pts. (2 At.) HO,SO^3, and 55 pts. (1 At.) $HO,C^4H^6O^2$, should, according to ordinary views, contain sulphovinic acid, hydrated sulphuric acid, and free alcohol:

$$2[2(HO,SO^3) + HO,C^4H^6O^2] = C^4H^6O^2,2SO^3 + 2(3HO,SO^3) + C^4H^6O^2.$$

But as no hydrochloric acid is formed on passing dry chlorine through the mixture (free alcohol immediately yields hydrochloric acid, but sulphovinic acid is not decomposed by chlorine), and as the boiling point is considerably higher than that of alcohol, it follows that all the alcohol must be combined with all the sulphuric acid, in the form of sulphovinic acid, and the water must be united with this compound, not with free sulphuric acid:

$$2(HO,SO^3) + HO,C^4H^6O^2 = C^4H^6O^2,2SO^3 + 3HO.$$

Also on mixing 2 At. HO,SO^3 with 1 At. $HO,C^4H^6O^2$ and 1 At. HO, a mixture is produced which does not boil below 140°, is not decomposed by chlorine, and must, therefore, be regarded as $C^4H^6O^2,2SO^3 + 4HO$. (Liebig, *Ann. Pharm.* 30, 129.)

With a larger quantity of water, no sulphovinic acid is formed at ordinary temperatures, but on the application of heat, its formation goes on: 98 pts. (1 At.) oil of vitriol, mixed with 36 pts. (4 At.), or 54 pts. (6 At.) water, and an indefinite quantity of alcohol, produce no sulphovinic acid at ordinary temperatures; but this mixture, when heated, yields nearly as much sulphovinic acid as oil of vitriol produces with alcohol alone; the sulphovinic acid may be obtained by neutralizing the

hot mixture with carbonate of lime. — Hence also the quantity of sulphovinic acid in mixtures of oil of vitriol and alcohol is increased by heating; for the dilute sulphuric acid produced in the cold, together with the sulphovinic acid, acts upon the remaining alcohol when heat is applied, and forms more sulphovinic acid.—Such a mixture of $2(HO,SO^3)$, $4HO$, and alcohol must, when heated, produce very dilute sulphuric acid, in addition to the sulphovinic acid. It therefore boils at a temperature below that of sulphovinic acid, giving off, first the water of the very dilute sulphuric acid together with free alcohol, and when the distillation has gone on so far that only $4HO$ are combined with $2SO^3$ (which compound boils between 136° and 141°), the sulphovinic acid is likewise decomposed (between 124° and 127°), and yields ether. (Liebig, *Ann. Pharm.* 9, 36.)

In the formation of sulphovinic acid, the sulphuric acid appears to act by its affinities for water and for alcohol simultaneously. One portion of the acid unites with alcohol to form sulphovinic acid, and its saturating power being thereby reduced one-half, it gives up half its combined water to the remaining portion of the oil of vitriol, till the latter is converted into terhydrated sulphuric acid:

$$5(HO,SO^3) + 2C^4H^6O^2 = 2(HO,C^4H^6O^2,2SO^3) + 3HO,SO^3.$$

This equation follows, at all events, from the experiments of Duflos, according to which, absolute alcohol converts 80 per cent. of sulphuric acid into sulphovinic, and from those of Millon, who found that absolute or 85 p. c. alcohol converts 77 per cent. of sulphuric acid into sulphovinic; in this result it is certainly remarkable that 85 p. c. alcohol should produce as much sulphovinic acid as absolute alcohol, although the quantity of sulphuric acid converted into the terhydrate must be greater in the former case than in the latter. Considering, however, the contradictory statements made by other observers, we cannot regard this equation as positively established, certainly not as true for all temperatures, inasmuch as Liebig found that more sulphovinic acid is produced at higher than at ordinary temperatures.

100 pts. of a mixture of equal parts of absolute alcohol and oil of vitriol should accordingly contain 55·102 pts. of $HO,C^4H^6O^2,2SO^3$, 13·673 pts. of $3HO, SO^3$, and 31·225 pts. of absolute alcohol in excess. But this excess of alcohol must be loosely combined with one or other of the two acids, since the boiling point of the mixture is above 100°, and, according to Liebig, no hydrochloric acid is formed by passing chlorine through it.

By heating the mixture of alcohol and sulphuric acid with excess of water, all the sulphovinic acid may be decomposed, the water breaking up the combination of the alcohol and sulphuric acid. When a mixture of alcohol and oil of vitriol is distilled, with frequent addition of water, all the alcohol passes over, and the residue no longer contains sulphovinic, but only dilute sulphuric acid. (Hennel.)

b. Formation of Ether and Water.

A mixture of 1 pt. alcohol and between 1 and 2 pts. oil of vitriol, heated in a distillatory apparatus, boils between 120° and 140°, at first giving off ether, together with more or less of undecomposed alcohol, then at 140° scarcely anything but ether, then at 160° ether with water, and at length, when, in consequence of this decomposition of the alcohol, the proportion of sulphuric acid has become excessive, and the temperature

rises above 160°, the mixture gives off sulphurous acid, olefiant gas, oil of wine, and other products hereafter to be considered, with which, up to 200°, a small quantity of ether still continues to distil over. If, however, the alcohol be allowed to flow constantly into the vessel so as to maintain the proportion of about 5 pts. alcohol to 9 pts. oil of vitriol (p. 172), neither sulphurous acid nor the subsequently mentioned products are formed (excepting a small quantity of sulphovinate of wine-oil), but the alcohol, as fast as it is supplied, is given off again in the form of water and ether, so that a given quantity of oil of vitriol is capable of converting a large quantity of alcohol into water and ether; the acid, however, constantly diminishes in etherifying power, so that a continually greater quantity of undecomposed alcohol passes over with the ether and water. The residue of the ether-preparation contains no sulphovinic acid, but only hydrated sulphuric acid.

a. Experiments with Oil of Vitriol and Absolute Alcohol.

Oil of vitriol and absolute alcohol, mixed in equal portions and heated, while fresh alcohol is admitted as fast as it is decomposed, yields at first a distillate of sp. gr. 0·768. The sp. gr. of the distillate then rises gradually, till the oil of vitriol is converted into bihydrated sulphuric acid, by addition of water derived from the alcohol, at which stage of the process the sp. gr. of the distillate becomes equal to that of the alcohol which flows in, and remains so. (Mitscherlich, *Pogg.* 31, 278.)

A mixture of 100 pts. (2 At.) oil of vitriol, and 47·31 pts. (1 At.) absolute alcohol boils at 100°, from that temperature till 165° gives off ether, and above 165°, sulphurous acid, &c. The ether amounts to 22 p. c. of the alcohol. With this proportion, and under the ordinary pressure, the boiling begins between 130° and 140°, and ether alone without any alcohol distils over from the beginning. But in a distillatory apparatus exhausted of air, and connected with a receiver surrounded with a freezing mixture, the mixture begins to boil at 86°, and from that temperature to 104°, one-fourth of the alcohol contained in the mixture distils over without any ether, and between 104° and 145°, white fumes are disengaged, which condense to an aromatic, sharp-tasting, colourless oil, and an aqueous solution of sulphurous acid. If air be then admitted into the apparatus, and the heating continued, not a trace of ether is obtained, but only sulphurous acid, &c. Hence, when the atmospheric pressure is removed, no ether is obtained, but first alcohol, and then at 104°, a sort of wine-oil, together with water und sulphurous acid. (Kuhlmann, *Ann. Pharm.* 33, 217 and 218.)

A mixture of oil of vitriol and absolute alcohol in equal portions, kept for some time at a temperature between 75° and 100°, yields a distillate of sp. gr. 0·817, consisting of a large quantity of alcohol, and a small quantity of ether. At 112°, it begins to boil slightly and in small bubbles, — ceasing, however, after a short time unless the heat be raised, — and between 111° and 116°, yields a distillate, of sp. gr. 0·792, containing a large quantity of ether, and a small quantity of alcohol; the following distillates also consist chiefly of ether with a little alcohol, but no water. When a mixture of 18 pts. oil of vitriol and 17 pts. absolute alcohol is kept for some time over the water-bath at a temperature not exceeding 100°, the distillates, if examined from time to time, exhibit the following variations of density and composition: *a.* Contains

1 pt. alcohol to 2 pts. ether; — *b.* 0·775 very pure ether, free from wine-oil; — *c.* 0·745 ether, with a layer of water below it; — *d.* The same. Hence it appears that ether is formed even below 100°; this distillation, however, is extremely slow, and even by the continued action of a temperature of 100°, it is impossible to obtain all the ether; in fact, out of the 35 parts of the mixture, only 4½ pts. of distillate pass over, and a residue is left amounting to 27 parts, and probably containing isethionic and ethionic acid, as well as hydrated sulphuric acid. (H. Rose & Wittstock, *Pogg.* 48, 463.) Compare also the experiments of the same chemists with very highly rectified spirit. (p. 229).

When alcohol and oil of vitriol are mixed in equal portions, in such a manner as to avoid all rise of temperature, and the mixture then rapidly heated to the boiling point, a distillate is obtained, even before the boiling heat is reached, consisting of: *a.* 0·776; — then at commencing ebullition: *b.* 0·808; — *c.* 0·800; — *d.* 0·786; — *e.* 0·776 (*a* and *e* are homogeneous mixtures of alcohol and ether); — then *f*, ether of 0·761, with a thin watery stratum below it; — then *g*, ether of 0·809 (containing wine-oil and sulphurous acid) with a watery stratum of equal thickness below it. Hence the ether gradually takes the place of the alcohol, and the water unites with the latter. (H. Rose & Wittstock.)

β. Experiments with Oil of Vitriol and Strong Spirit.

Oil of vitriol of sp. gr. 1·665 [1·865 ?] and alcohol of 40° Bm. suddenly mixed (whereupon the temperature rises to 106°) and then distilled, yield first alcohol, amounting to $\frac{1}{20}$ of the original quantity; then a mixture of alcohol and ether; then, when the residue has given off at least $\frac{1}{4}$ of its alcohol, ether free from alcohol is evolved, and continues to pass over till only half the original quantity of alcohol is left in the residue. If the heat be then continued and alcohol allowed slowly to flow in to the residue, so as never to let the quantity of oil of vitriol in the residue exceed $\frac{2}{3}$ of the whole, ether still continues to pass over, and a reddish residue is left. If water be suffered to flow in instead of alcohol, the distillate consists of water, with only a small quantity of ether. When a slowly prepared mixture of oil of vitriol of 65½° Bm. and an equal quantity of alcohol of 40° Bm. is quickly heated to the boiling point, till ether begins to pass over, the retort then cooled with wet cloths, and the colourless residue, which smells strongly of ether, neutralized by potash, the mixture, when distilled to dryness, leaves a non-blackened residue, and yields a distillate which, besides alcohol, contains a quantity of ether amounting to 23 per cent. of the alcohol used. When 2 pts. of oil of vitriol are quickly mixed with 1 pt. alcohol of 40° Bm. the yellowish brown mixture becomes heated to 110°, and exhibits, in addition to the odour of alcohol, an ethereal odour, which, after a few hours, is replaced by a bituminous odour, the liquid at the same time assuming a dark brown colour. When distilled, it yields a small quantity of ether, then sulphurous acid, wine-oil, &c. (Boullay, *J. Pharm.* 1, 106.)

When a mixture of equal parts of alcohol and oil of vitriol is heated for some time in an open basin, and then left to cool, the ether-vapour which is given off being continually blown away, to prevent any ether that may be condensed from flowing back into the residue, this residue, if mixed with water, still gives off ether-vapour with effervescence.

Hence the heated mixture contains ether ready formed, but held back with a certain force; it is, however, driven out on boiling. (Mitscherlich, *Lehrb.* Aufl. 4, 1, 246.)

A mixture of equal parts of alcohol and oil of vitriol gives off at first undecomposed alcohol; with 2 pts. oil of vitriol and 1 pt. alcohol, nothing passes over at first but ether and water. The best proportion for the formation of ether is 4 pts. oil of vitriol to 3 pts. alcohol. (Geiger.) If a mixture of 9·6 pts. oil of vitriol and 7·2 pts. alcohol of sp. gr. 0·842 be distilled, with continual admission of fresh alcohol, till the distillate amounts to 57·6 pts. (and therefore 46 pts. [1 At.] of absolute alcohol have been used), that distillate will contain 40·8 pts. of crude, or about 33·6 pts. of pure ether (if all the alcohol which passes over had been decomposed, the quantity of ether would have amounted to 37 pts. [1 At.]). The brownish transparent residue in the retort, amounting to 13·2 pts. contains sulphuric acid, water, and ether, and yields, when saturated with carbonate of baryta, nothing but sulphate of baryta, quite free from sulphovinate. (Geiger, *Repert.* 11, 85.)

Oil of vitriol of sp. gr. 1·920 [1·820 ?] yields, with an equal quantity of alcohol which boils at 82·5°, a mixture whose boiling point is 115°. (Duflos, *Berl. Jahrb.* 27, 1, 76.)

A mixture of 3 pts. oil of vitriol and 2 pts. strong alcohol (which contains a considerable quantity of sulphovinic acid) begins to emit an odour of ether at 120° or 122°, and boils fully at 131°, assuming at the same time a brown colour. If alcohol be then admitted so as to cool the mixture to 119°, the formation of ether continues. If the operation be now interrupted, the residue still contains sulphovinic acid. If, on the other hand, a similar mixture be kept at 112°—118° till the residue contains 2 pts. oil of vitriol to 1 pt. alcohol, and then quickly heated to its boiling point, viz. to 144°, at which temperature ether, sulphurous acid and wine-oil are evolved, — and if alcohol be then allowed to run in, and the heat maintained for half an hour between 137° and 140°, — whereupon ether passes over, mixed with continually decreasing quantities of sulphurous acid and wine-oil, — a residue is ultimately left which does not contain sulphovinic acid. If this residue be kept boiling for a still longer time without admitting fresh alcohol, a small quantity of water passes over, together with a large quantity of sulphurous acid, besides sulphuric, acetic, and carbonic acid, and olefiant gas. Hence the sulphovinic acid formed at a comparatively low temperature is decomposed at 140°, and the residue is often free from sulphovinic acid. (Duflos, *Kastn. Arch.* 12, 170; 14, 301.)

A small quantity of sulphovinic acid passes over at first together with the ether; and lastly, when sulphurous acid begins to escape, sulphovinate of wine-oil goes over, remaining behind when the last portions of ether in the distillate have evaporated. The wine-oil is not formed till the distillation has arrived at this stage; for if this compound be actually added to the mixture of alcohol and oil of vitriol, it immediately passes over; and if an ether-distillation be interrupted before sulphuric acid begins to escape, the residue, after cooling, agitated with ether, and the ether poured off and evaporated, not a trace of wine-oil is left behind. The olefiant gas is evolved simultaneously with the sulphurous acid and the wine-oil, or even somewhat before them. (Serullas, *Schw.* 55, 161.)

A mixture of equal parts of oil of vitriol and 85 per cent. alcohol begins to boil between 112° and 124°, first giving off alcohol; between

124° and 127° it yields alcohol and ether, then between 127° and 160° ether and water, after which the mixture blackens and gives off sulphurous acid, &c. (Liebig.)

In a mixture of 147 pts. (3 At.) oil of vitriol and 110 pts. (2 At.) 85 per cent. alcohol, which contains 1 At. of absolute alcohol to 1 At. water, the substances present are : $3SO^3+2C^4H^6O^2+5HO=HO,C^4H^6O^2,2SO^3+4HO,SO^3+C^4H^6O^2$. This mixture begins to boil at 130°, yielding ether mixed with a very small quantity of alcohol, and, as the temperature rises, also with water. The hydrated sulphovinic acid, $HO,C^4H^6O^2,2SO^3$, may be supposed to be resolved into ether and oil of vitriol $=C^4H^5O+2\ (HO,SO^3)$. Liebig (*Ann. Pharm.* 9, 1; also *Pogg.* 31, 320.)

A slowly prepared mixture of oil of vitriol with an equal quantity of 90 per cent. alcohol, distilled in the water-bath, yields first a distillate of sp. gr. 0·833, consisting almost wholly of alcohol ; then distillates of sp. gr. 0·787 and 0·789, which are almost all ether; and subsequently ether mixed with water. When the alcohol used in the preparation is hydrated, a larger proportion of it passes over undecomposed at the beginning of the distillation than when it is absolute, because the former is less completely converted into sulphovinic acid [or because the water in the hydrated alcohol weakens the sulphuric acid]. Ether always contains wine-oil unless it be distilled below 100°, in which case only the last distillates contain traces of that compound; hence the formation of wine-oil requires either a temperature above 100°, or long-continued exposure to 100°. The residue in the retort has but a very slight brownish colour, and does not smell of sulphurous acid. (H. Rose & Wittstock.)

A mixture of equal parts of oil of vitriol and alcohol of sp. gr. 0·820 distilled till the greater part of the ether has passed over, but not till the liquid in the retort blackens, contains afterwards only $\frac{2}{3}$ or $\frac{3}{4}$ of the sulphovinic acid which existed in it before distillation. (Hennel.)

When 3 pts. of oil of vitriol are distilled with 32 pts. of strong alcohol, no ether is obtained, not even when the right proportion between the oil of vitriol and alcohol exists in the residue. This effect cannot arise from weakening of the oil of vitriol by the water of the alcohol ; for the alcohol which passes over is a degree weaker than it was originally. (Büchner, *Br. Arch.* 24, 301.)

γ. *Experiments with Oil of Vitriol and Weak Spirit.*

4 parts of oil of vitriol, 2 pts. of very highly rectified spirit, and 1 pt. water, yield by distillation a mixture of ether with a large quantity of alcohol. — With 2 : 1 : 1, no ether is obtained, but only weak spirit, which distils over so completely that the residue is scarcely browned by continuing the distillation. (Deslauriers, *J. Pharm.* 2, 483.)

When 100 pts. oil of vitriol are mixed, first with 20 pts. water, then with 50 pts. absolute alcohol, and distilled, absolute alcohol being allowed to flow in at such a rate as to keep the volume of the mixture the same, and the boiling point constantly at 140°, the specific gravity of the distillate, which is at first 0·780, gradually rises to 0·798, and afterwards remains the same throughout the distillation. At first it is somewhat less, because the oil of vitriol still takes up a small quantity of water, but afterwards it remains constantly equal to that of the alcohol which runs in. In this manner any quantity of ether may be prepared; for the sulphuric acid remains unaltered, excepting that a small quantity of it volatilizes or is decomposed by foreign bodies in the alcohol. 100 parts

of the distillate (which forms two layers) contain 65 pts. ether, 17 water, and 18 alcohol. — If 3 pts. oil of vitriol be mixed with 2 pts. water and with absolute alcohol, and absolute alcohol allowed to flow in during the boiling, aqueous alcohol of 0·926 passes over first, with scarcely a trace of ether; the specific gravity of the distillate then sinks gradually to 0·885, and ultimately becomes equal to that of the absolute alcohol which runs in. — A mixture of equal parts of absolute alcohol and oil of vitriol, mixed with a large quantity of water, allows nearly all the alcohol to pass over undecomposed, no ether being formed till the boiling point has risen to 126°. (Mitscherlich, *Pogg.* 31, 322.)

If the oil of vitriol be mixed with a sufficient quantity of water to make it boil at 145°, and vapour of alcohol of 100° passed into it while it is boiling in the distillatory apparatus, ether, water, and $\frac{1}{5}$ undecomposed alcohol pass over. A heat which would bring the mixture to 130°, if no alcohol vapour were introduced, is sufficient, under the circumstances of the experiment, to raise it to 145°, because the alcohol gives out heat, not only from the condensation of its vapour by the sulphuric acid, but likewise when it separates into ether and water; and these quantities of heat are together greater than that which is rendered latent by the evaporation of the alcohol. When liquid alcohol is allowed to run into the mixture, it may cool the liquid at the point where it enters; and we may then suppose (with H. Rose) that sulphovinic acid is formed at that particular point, and, diffusing itself through the latter mixture, is resolved into ether and hydrated sulphuric acid; when, on the contrary, the alcohol is passed into the liquid in the state of vapour, the mixture becomes heated. Moreover, a certain quantity of sulphovinic acid is found in the mixture during the whole operation; this, however, can only be regarded as a secondary product, for we cannot suppose that it is produced and destroyed at the same temperature. (Mitscherlich, *N. Ann. Chim. Phys.* 7, 12; also *Lehrb.*)

100 pts. oil of vitriol mixed with 100 pts. alcohol, and set aside for a few days, — then mixed with 200 pts. water, and distilled till 280 pts. have passed over, yield neither ether nor sulphurous acid, nearly all the alcohol and the sulphuric acid being recovered in their original state, — either because the water decomposes the sulphovinic acid by depriving it of all its sulphuric acid, or because the water prevents the temperature from rising high enough. (Hennel.)

A mixture of 100 pts. (2 At.) oil of vitriol, $18\frac{1}{8}$ pts. (2 At.) water, and 48 pts. (1 At.) absolute alcohol ($= 2SO^3 + C^4H^5O + 5HO$) does not contain any free alcohol; for, when dry chlorine is passed through it, no hydrochloric acid is formed, and it does not boil below 140°; the distillate which it yields has a density of 0·778, and contains 21·43 pts. water to 100 ether. — A mixture of 100 pts. (2 At.) oil of vitriol, 48 pts. (1 At.) alcohol, and 27 pts. (3 At.) water ($= 2SO^3 + C^4H^5O + 6HO$) yields a distillate which has a specific gravity of 0·797, and contains 22 pts. water to 100 ether. — When a mixture of 9 pts. oil of vitriol and 5 pts. alcohol is mixed with a sufficient quantity of water to depress the boiling point below 126°, no ether passes over but only alcohol. (Liebig.)

Theory of Etherification by Oil of Vitriol.

The final result of the action of about 9 pts. oil of vitriol on 5 pts. of strong alcohol between the temperatures of 120° and 150°, is always the resolution of the alcohol into ether and water, which pass over, while the oil of vitriol remains behind in combination with a larger quantity of water than before, and partly also converted into sulphovinic acid. We may therefore say generally that alcohol, by the action of sulphuric acid, is resolved into ether and water, either as expressed by the formula $C^4H^6O^2 = C^4H^5O + HO$, or, if the atomic weight of ether be taken twice as great, according to the formula, $2C^4H^6O^2 = C^8H^{10}O^2 + 2HO$. That ether is alcohol *minus* water was first shown by Gay-Lussac (*Ann. Chim.* 95, 311.) It is true that Fourcroy and Vauquelin had previously supposed that sulphuric acid converts alcohol into ether by abstraction of water; but they also imagined that the strong heat required to boil the mixture of alcohol and oil of vitriol causes a separation of charcoal, and accordingly that ether is alcohol *minus* water and *minus* carbon.

But, though chemists are agreed respecting the final result of this action, they nevertheless differ in their views regarding the cause of the resolution of the alcohol into water and ether, and the nature of the transformation which precedes this decomposition. Is the force by which the alcohol is resolved into ether and water, chemical or catalytic? Does the sulphuric acid decompose the alcohol immediately into ether and water, or does it first unite with the alcohol, forming sulphovinic acid, which then yields the ether by decomposition?

The majority of chemists, *e.g.*, Hennel, Serullas, Liebig, Magnus, H. Rose, Dumas, Graham [compare however p. 233], Gerhardt, and others, are inclined to suppose that chemical force is the cause of the decomposition, and that sulphovinic acid is produced in the first instance, and afterwards resolved into ether and sulphuric acid. This view is supported by Hennel's statement that sulphuric acid diluted with so much water that it will not form sulphovinic acid with alcohol, is likewise incapable of converting the alcohol into ether by distillation, and that the quantity of sulphovinic acid in a mixture of alcohol and sulphuric acid continually decreases as the distillation of the ether proceeds.

A mixture of oil of vitriol with at most an equal quantity of alcohol may be supposed to contain monohydrated sulphovinic acid, $HO,C^4H^6O^2,2SO^3$, dilute sulphuric acid (perhaps $3HO,SO^3$) and loosely combined alcohol, and the sulphovinic acid may be supposed to be resolved by heat into ether and oil of vitriol:

$$HO,C^4H^6O^2,2SO^3 = C^4H^5O + 2(HO,SO^3).$$

The oil of vitriol forms, with the terhydrated sulphuric acid, an acid of medium strength, which becomes continually stronger by evaporation of water, and remains in the retort together with the loosely combined alcohol.

As ether is constantly formed so long as alcohol is continually admitted to the boiling mixture, we must suppose that the formation of sulphovinic acid likewise goes on continually, preceding that of the ether. We are hereby compelled to admit that, in the same mixture, sulphovinic acid is continually produced and decomposed. This difficulty is not obviated by supposing that, at the higher temperature, sulphovinic acid is no longer formed, but the sulphuric acid abstracts HO

directly from the alcohol, and thereby liberates the ether; for it is equally difficult to understand how the sulphuric acid, at the very temperature at which it takes HO from the alcohol, can also give off this HO together with the ether vapour.

Liebig (*Pogg.* 31, 350) endeavours to remove this difficulty in the following manner: The temperature at which sulphovinic acid decomposes is not much below that at which the dilute sulphuric acid in the mixture would give off vapour of water; for $3\,HO,SO^3$ boils between 163° and 170°, $4HO,SO^3$ between 136° and 141°, and $5HO,SO^3$ between 118° and 122°; the formation of ether begins at 124°, and is most abundant at 140°, at which temperature alcohol is no longer evolved, but only ether and water. No water can be evolved from that part of the liquid where the ether vapour is set free by the decomposition of the sulphovinic acid, because oil of vitriol is there set free; but as the bubbles of ether rise through the liquid, the ether vapour takes up a quantity of aqueous vapour corresponding to its temperature (I, 266), this water being abstracted from the dilute sulphuric acid in the mixture, and thus ether and water distil over together.

This explanation certainly serves to show how ether and water may be evolved together, but it is still not satisfactorily made out how fresh portions of sulphovinic acid can be formed at the very temperature at which that compound is decomposed,—a point to which attention has also been called by Masson (*Ann. Chim. Phys.* 69, 226). H. Rose observes, indeed, that at the point where the alcohol runs in, the mixture becomes cooled, and thus fresh sulphovinic acid may be formed, and afterwards decomposed as it spreads through the hot mixture. The insufficiency of this explanation is however shown by Mitscherlich's experiment (pp. 229, 230), in which, when alcohol was passed in the form of *vapour* into a mixture of oil of vitriol and water boiling at 145°, ether and water were continually produced, although at the part of the mixture where the alcohol enters, a great rise instead of a fall of temperature must be produced by the condensation of the vapour. This material difficulty in the assumption that ether is formed from sulphovinic acid is therefore not yet removed; but as all other circumstances tend rather to support this theory than any other, it is to be hoped that the obscurity will be cleared up by further investigations. For the present we may remark that the alcohol vapour acts in excess at that particular part of the liquid where it enters, and may therefore be able, even at 145°, partially to expel the water from the surrounding hydrated sulphuric acid, and form sulphovinic acid, which then, as it diffuses through the rest of the liquid, where the hydrated sulphuric acid is in excess, is again resolved into ether and oil of vitriol. These comparatively loose and nearly equal affinities of water and alcohol for sulphuric acid, are in accordance with Berthollet's law of the partition of the sulphuric acid between the water and the alcohol, in proportion to the chemical masses of those two bodies actually present at the point where the alcohol enters the liquid; and it is perfectly consistent with this theory that part of the alcohol should remain uncombined,—in fact, as Mitscherlich found, that $\frac{1}{5}$ of the alcohol which enters, should pass off uncombined, together with the ether vapour. In general, no fixed degree of heat can be assigned as that at which the decomposition of sulphovinic acid takes place under all circumstances. The concentrated acid in the pure state decomposes even at a gentle heat. In a mixture of equal parts of oil of vitriol and alcohol, the decomposition begins between 127° and 160°; but the portions of sulphovinic acid which remain mixed with

the strong sulphuric acid in the residue do not decompose till they are more strongly heated. Hence concentrated sulphuric acid appears to retard the decomposition of sulphovinic acid by heat, a circumstance which seems to indicate a combination between the two acids.

Whether that portion of the alcohol, which is present in a mixture of equal parts of alcohol and oil of vitriol without being converted into sulphovinic acid, does subsequently, after the decomposition of part of the sulphovinic acid, yield more sulphovinic acid and afterwards ether,—is a question not yet determined with certainty: for such mixtures, and even those which contain a larger proportion of oil of vitriol, give off a large quantity of alcohol as well as ether. Further, if it be considered that the heated mixture contains more sulphovinic acid than the same mixture when cold, and therefore that the quantity of free alcohol is diminished by heating, it appears possible that all the free alcohol in the heated mixture may distil over unaltered. If it should appear that even this portion is, in the course of the distillation, converted into sulphovinic acid and then into ether, the explanation last given, viz., that the alcohol must act in excess at particular points of the mixture, to form fresh sulphovinic acid, must certainly be regarded as inadmissible.

According to this theory, the formation of ether by sulphuric acid is in accordance with its formation by the action of phosphoric, arsenic, perchloric acid, fluoride of boron, chloride of zinc, protochloride of tin, &c. All these substances enter into intimate combination *both with water and with alcohol.* Sulphuric, phosphoric, and arsenic acid, produce sulphovinic, phosphovinic, and arseniovinic acids; and although the compounds of the other substances above-mentioned have less decided characters, they nevertheless require a strong heat to decompose them, and when thus decomposed, give off—in consequence of the affinity of the increased heat for the ether, and of the above-mentioned substances for water (whereby the affinity is overcome which holds together the elements of the ether and water in the form of alcohol) — part of the alcohol as ether, whilst the remainder is held back in the form of water or of its constituents.

The examples of chloride of zinc and chloride of tin show that the power of forming ether is by no means confined to the acid (or the so-called electronegative) bodies. That chloride of calcium does not likewise form ether, appears to be due to the circumstance that it gives off the alcohol at about 120°; still less can the formation of ether be brought about by many salts deprived of their water of crystallization, most of these salts in fact retaining water with great tenacity, but giving off alcohol with facility. With fixed alkalis, a peculiar effect is obtained. (vid. *Compounds of Alcohol.*) Against this might certainly be alleged the experiment of H. Rose and Wittstock (p. 227) according to which a mixture of alcohol and oil of vitriol gives off a small quantity of ether even below 100°. Perhaps in this case the adhesion of the air and of the evolved alcohol vapour to the ether vapour, gives rise to the production of a mixture of air, alcohol vapour, and ether vapour. That, however, a certain elevation of temperature is required for the formation of ether, is shewn by Kuhlmann's experiment (p. 226) according to which oil of vitriol heated with absolute alcohol in vacuo does not form ether, but first alcohol and then oil of wine.

Theories of etherification, also founded on affinity, but differing from the preceding, have been given by Sertürner (*Kastn. Arch.* 7, 436); — Gay-Lussac (*Ann. Chim. Phys.* 13, 78); — Thénard (*Traité de Chim.* ed. 4, 4, 146); — Heeren (*Pogg.* 7, 198); — Von

Mons (*Taschenb.* 1822, 175); — Dulk (*Berl. Jahrb.* 29, 1, 11); — Geiger (*Repert.* 11, 58); — Fechner (*Schw.* 49, 75; 52, 92); — Dumas & Boullay (*J. Pharm.* 14, 10); — Graham (*Lehrb.*)

Mitscherlich's *Contact Theory* simply assumes that sulphuric acid, without being decomposed or entering into combination, has at high temperatures the power of separating alcohol into ether and water (vid. *Catalytic force* I, 114 — 117.) Mere heat is not capable of effecting this decomposition of alcohol, for the alcohol, when passod through a red-hot tube, does not yield ether. The presence of a contact-substance is necessary, and this substance must be electro-negative [but what with regard to chloride of zinc?]. The sulphovinic acid is merely a secondary product, and by no means essential to the formation of ether. Neither aqueous sulphovinic acid nor its salts yield ether when heated. [Compare, however, *Sulphovinic acid.*] (Mitscherlich, *Lehrb.* Aufl. 4, 1, 247 and 255.) — This mode of viewing the matter certainly removes a great many difficulties, but instead of an explanation of the process, merely gives it a name, which cannot be regarded as satisfactory (Gm.) — If the sulphovinic acid formed in a mixture of 100 pts. oil of vitriol and 55 pts. of 85 per cent. alcohol has nothing to do with the formation of ether, but that process depends entirely upon the still uncombined alcohol, the quantity of which (even if we suppose that only $\frac{2}{3}$ of the sulphuric acid has been converted into sulphovinic acid, and $\frac{1}{3}$ into dilute sulphuric acid) amounts to only 13·3 pts., such a mixture could yield only 8·8 pts. of ether, whereas if the distillation be continued till the residue begins to decompose, 30 pts. of ether and 9 pts. of alcohol are obtained. [There is probably a misprint in the passage from which this is extracted; a considerable quantity of alcohol always remains in the residue, and makes the quantity of ether produced appear too large.] A mixture of 100 pts. oil of vitriol, 40 pts. water, and 50 pts. alcohol, enclosed in a sealed tube, and exposed for several hours to a temperature of 140°, does not produce a trace of ether. (Liebig, *Handworterbuch*, 1, 115.)

¶ Graham takes a similar view of the process of etherification; he finds that ether may be produced by merely heating alcohol and oil of vitriol together, without distillation, as in the following experiments: — 1 vol. oil of vitriol was mixed gradually, so as to avoid any great rise of temperature, with 4 vol. alcohol of sp. gr. 0·841, containing 83 per cent. of absolute alcohol (the same was also used in the subsequent experiments), and the mixture introduced into a strong glass tube, which was then sealed and heated for an hour to 140° — 178°; the liquid, after cooling, occupied a larger space than before it was heated, and was divided into two layers, the upper consisting of ether free from sulphurous acid, while the lower, which was twice as deep, and had a slight yellowish colour, contained a small quantity of ether, but consisted chiefly of alcohol, water, and sulphuric acid, without any perceptible quantity of sulphovinic acid. — When 1 vol. oil of vitriol and 2 vols. alcohol of the same strength were heated together in a similar manner, the mixture turned brown and yielded but a small quantity of ether. — Equal volumes of oil of vitriol and alcohol formed a black, viscid liquid, but no perceptible quantity of ether. — When 1 vol. oil of vitriol and 8 vol. of the same alcohol were heated for an hour to 140° — 158°, an ethereal and a lower stratum of liquid were also formed in the proportion of 1·2; the quantity of ether was not increased by again heating the mixture for an hour to the same temperature. — When 1 vol. oil of vitriol and 4 vol. alcohol (as in the first experiment), were heated to 158° for an hour, ether and a lower acid

liquid were formed in the proportion by volume of 1·1 : 2·65; the latter was slightly yellowish, and contained but a small quantity of sulphovinic acid (when neutralized with lime, it yielded only 4·9 pts. sulphovinate of lime to 83·1 pts. sulphate.) — A mixture of 100 pts. oil of vitriol, 48 pts. alcohol of the above strength, and 18·5 pts. water heated for an hour to 143°, formed a dark greenish brown liquid, but no layer of ether. One half of this liquid mixed with half its bulk of water, and heated in a similar manner, yielded but a very small quantity of ether; the other half mixed with half its bulk of alcohol, and heated in a similar manner, yielded a quantity of ether measuring about half as much as the alcohol added. — Crystals of bisulphate of soda retaining a slight excess of acid heated in a similar manner with twice their volume of alcohol, converted it into ether; pure crystals of the same salt exhibited a perceptible but smaller power of converting alcohol into ether. Glacial phosphoric acid and crystallized phosphate of soda heated with alcohol to 182°, did not convert the smallest quantity of it into ether. Chloride of zinc similarly treated produced but a trace of ether, perceptible by the odour.

From these experiments, Graham concludes that sulphovinic acid does not yield ether, either by spontaneous decomposition or by its action in water; but that it produces that compound when it acts upon alcohol, just as other acid salts of sulphuric acid do. He further concludes that the action of the oil of vitriol on the alcohol consists in a doubling of the atomic weight of the hydrocarbon (C^4H^4) contained therein; — [alcohol $= C^4H^4,H^2O^2$; ether $= C^8H^8,H^2O^2$], — in other words, that it is a *polymerizing action*, similar to that which takes place when sulphuric acid is placed in contact with 20 times its volume of oil of turpentine, the turpentine being then converted into two other hydrocarbons, terebene and colophene, one of which has a much higher boiling point and greater vapour-density than the oil of turpentine. — Graham is also of opinion, that the formation of sulphovinic acid is not a necessary step in the production of ether; for in the preceding experiments, the etherizing proceeded most advantageously with bisulphate of soda, or with sulphuric acid mixed with a large proportion of alcohol and water, which would greatly impede the formation of sulphovinic acid. It appears indeed that the combination of alcohol with sulphuric acid in the form of sulphovinic acid, greatly diminishes the chance of the alcohol being afterwards etherized; for when the proportion of oil of vitriol was increased in the preceding experiments, which would give much sulphovinic acid, the proportion of ether rapidly diminished. — The process of etherification by sulphuric acid is then, as Mitscherlich considered it, an action of contact. (Graham, *Chem. Soc. Qu.* 3, 24 — 28.)

According to Williamson, on the other hand, the production of ether in the ordinary process of etherification is preceded by, and depends essentially upon, the formation of sulphovinic acid. — One atom of alcohol and 1 atom of oil of vitriol form 1 atom of sulphovinic acid (equivalents, VII, 27; comp. also VII, 223):

$$\left.\begin{matrix}C^2H^5\\H\end{matrix}\right\}O + \left.\begin{matrix}H\\H\end{matrix}\right\}SO^4 = \left.\begin{matrix}H\\H\end{matrix}\right\}O + \left.\begin{matrix}C^2H^5\\H\end{matrix}\right\}SO^4;$$

and this sulphovinic acid coming in contact with another atom of alcohol, yields sulphuric acid and ether:

$$\left.\begin{matrix}C^2H^5\\H\end{matrix}\right\}SO^4 + \left.\begin{matrix}C^2H^5\\H\end{matrix}\right\}O = \left.\begin{matrix}H\\H\end{matrix}\right\}SO^4 + \left.\begin{matrix}C^2H^5\\C^2H^5\end{matrix}\right\}O.$$

The sulphuric acid is thus reproduced, and the same series of actions continually repeated.

In this view of the process of etherification, we seem again to encounter the old difficulty of sulphovinic acid being first formed and then decomposed, at the same temperature and under the same circumstances. Williamson, however, regards the interchange of ethyl and hydrogen between C^2H^6O and H^2SO^4, and the subsequent interchange of the same elements between $C^2H^6SO^4$ and C^2H^6O, as merely a particular case of a general law of atomic motion, applicable to all cases of chemical decomposition whatsoever. He supposes, in fact, that the ultimate atoms of all bodies are in constant motion, continually changing places with each other, whether they be similar or dissimilar. Thus, in a drop of hydrochloric acid, HCl, each atom of H does not remain quietly in juxtaposition with the atom of Cl with which it is first united, but is constantly changing places with other atoms of hydrogen, or, what is the same thing, continually coming in contact with fresh atoms of chlorine. This change is not directly sensible to observation, because one atom of hydrochloric acid is exactly like another. But suppose we mix with the hydrochloric acid some sulphate of copper (the component atoms of which are undergoing a similar change of place); the basylous elements, hydrogen and copper, will then no longer limit their change of place to the circle of the atoms with which they were at first combined, but the hydrogen and copper will likewise change places with each other, forming chloride of copper and sulphuric acid. Thus it is that in this and similar cases, the bases are divided between the acids. If, however, one of the new compounds formed be insoluble in the liquid, as when sulphate of silver is substituted for the sulphate of copper, in which case the compounds formed are H^2SO^4, Ag^2SO^4, HCl and AgCl, — the insoluble compound (the AgCl in the present instance) is precipitated, and thereby removed from the circle of decompositions, while the other three compounds remaining in solution, continue the interchange of their component parts, and give rise successively to new portions of chloride of silver, until all the silver, or all the chlorine, is removed from the liquid. Such indeed is the general process of chemical decomposition. Of course a compound is as effectually removed from the circle of decompositions by assuming the gaseous form as by precipitation; and thus it is that in the process of etherification by sulphuric acid, the ether and water being removed from the liquid by distillation as fast as they are produced, the sulphuric acid continues to act upon the alcohol as long as the supply of that compound is kept up. (*Chem. Soc. Qu. J.* 4, 109, 112.)

The view just given of the process of etherification is confirmed by the following experiments. When sulphamylic acid $\left.\begin{matrix}C^5H^{11}\\H\end{matrix}\right\}SO^4$ was heated in a retort, and a stream of common alcohol allowed to run in till nothing but common ether passed over, the distillate was likewise found to contain amylovinic ether $\left.\begin{matrix}C^5H^{11}\\C^2H^5\end{matrix}\right\}O$, and the residue contained no sulphamylic acid, but only sulphovinic. Again, on distilling a mixture of common and amylic alcohol in equivalent proportions with sulphuric acid, amylovinic ether was formed, as well as common ether and amylic ether. A mixture of methylic and amylic alcohols similarly treated, yielded amylomethylic ether, $\left.\begin{matrix}C^5H^{11}\\C\ H^3\end{matrix}\right\}O$. (Williamson, *Chem. Soc. Qu. J.* 4, 229.)

These views are also confirmed by the experiments of Chancel (*Laur. & Gerh. Compt. rend.* 1850, 369), who finds that anhydrous sulphovinate

first to be converted into isethionic acid, and ultimately into hydrated sulphuric acid. (Liebig.)

Equal parts of oil of vitriol and absolute alcohol yield ether and water at 165°, then water, then a large quantity of sulphurous acid, olefiant gas, wine-oil, and a small quantity of acetic acid. At 180° the residue froths up. (Kuhlmann, *Ann. Pharm.* 33, 217.)

The mixture of equal parts of alcohol and oil of vitriol yields between 120° and 150°, alcohol, ether, and water; between 150° and 160, merely ether and water; between 160° and 165°, sulphurous acid, olefiant gas and carbonic acid, together with a small quantity of ether; at 175°, the ether disappears altogether, but water and sulphovinate of wine-oil are given off as well as the above-mentioned gases. The gaseous mixture contains sulphurous acid and olefiant gases in about equal volumes, and likewise carbonic acid gas, amounting to between $\frac{1}{6}$ and $\frac{1}{3}$ of the olefiant gas. Finally, there remain hydrated sulphuric acid, isethionic acid, and charcoal impregnated with sulphuric acid. (Marchand, *J. pr. Chem.* 15, 13.)

Scheele obtained no carbonic acid; Proust (*A. Gehl.* 3, 41) obtained neither acetic acid nor sulphur; Duflos obtained not only acetic acid but likewise acetate of ethyl. The carbonic oxide was first noticed by J. Davy (*Ed. J. of Sc.* 6 43), and afterwards by Regnault (*Ann. Chim. Phys.* 69, 168), (comp. p. 163).

One ounce of alcohol of sp. gr. 0·8 heated with 4 ounces of oil of vitriol, as long as any gas escapes, yields, after the sulphurous acid and ether-vapour have been absorbed by water, $11\frac{1}{4}$ litres of a gaseous mixture. The first $\frac{5}{15}$ of the evolved gas consist of olefiant gas free from carbonic oxide, but containing a small quantity of carbonic acid, which occurs even in the first $\frac{1}{15}$, and gradually increases as the process goes on; the next $\frac{5}{15}$ are olefiant gas with a larger proportion of carbonic acid, and not more than 4 per cent. of carbonic oxide. In the eleventh and twelfth $\frac{1}{15}$, the carbonic acid and carbonic oxide gases exhibit a considerable increase; and the thirteenth, fourteenth, and fifteenth $\frac{1}{15}$ consist, for the most part, of carbonic oxide, mixed with a considerable quantity of carbonic acid and a small proportion of sulphurous acid, the olefiant gas having by this time, almost wholly disappeared. (A. Vogel, Junior, *J. pr. Chem.* 25, 300.) — Faraday thought that he likewise obtained marsh-gas (p. 163).

When vapour of absolute alcohol is passed into oil of vitriol contained in a tubulated retort, sulphurous acid and olefiant gases are evolved, water and oil of wine distil over, and in the retort there remain hydrated sulphuric acid, isethionic acid, and thiomelanic acid, which separates out and thickens the mass. (Lose, *Pogg.* 47, 619.)

When vapour of 80 per cent. alcohol is passed through a mixture of 10 pts. oil of vitiol and 3 pts. water boiling between 160° and 165°, the alcohol is almost wholly resolved into olefiant gas and vapour of water, mixed only with a little vapour of alcohol and a very small quantity of ether-vapour. The acid liquid remains colourless, and after the experiment has continued for a long time, deposits charcoal, especially when the heat rises above 170°; these products of carbonization are, therefore, not essential to the formation of the olefiant gas. The sulphuric acid which, at a lower temperature, decomposes the alcohol by contact-action into ether and water, resolves it at 160°, also by mere contact-action, into olefiant gas and water. (Mitscherlich, *N. Ann. Chim. Phys.* 7, 12; also *Lehrb.* Aufl. 4, 1, 195.)

ately yield carbonic oxide by decomposition. — 4. The sulphur which sublimes on heating the residue to dryness is probably derived from the decomposition of thiomelanic acid.

Thiomelanic Acid.

G. Bischof. *Schw.* 41, 419. — Erdmann & Marchand, *J. pr. Chem.* 15, 13. — Lose, *Pogg.* 47, 619. — Erdmann, *J. pr. Chem.* 21, 291; also *Ann. Pharm.* 37, 82.

This is the carbonaceous mass containing sulphuric acid, which separates out when alcohol is strongly heated with oil of vitriol. As its composition is not yet known with certainty, it is perhaps best introduced in this place.

Preparation. Vapour of absolute alcohol is passed into a tubulated retort half filled with rectified oil of vitriol, and heated to 160° till the mass thickens; the whole is then diluted with water, and the carbonaceous mass washed for several days with hot water, till the liquid which runs through no longer forms a cloud with chloride of barium. It then swells up strongly, and finally dissolves in small quantity, imparting a brownish colour to the water. (Lose.) Erdmann proceeds in a similar manner, excepting that he also digests it with ammonia.

2. *a.* 1 pt. of absolute alcohol is heated in a sand-bath with 8 to 10 pts. of [rectified?] oil of vitriol till the residue assumes the form of spongy lumps. These lumps are then washed out of the retort with water, as long as the water continues to take up sulphuric acid; the residue triturated with water to a very fine cream; and afterwards repeatedly washed with water, which still takes up a considerable quantity of sulphuric acid from it. (Erdmann.) — *b.* The same process, excepting that the heat is raised above 180°, till the mass begins to thicken. (Erdmann.)

Properties. Thiomelanic acid in the dry state is a pure black, porous mass, having a shining fracture. (Lose.) — Dull on the outside, but lustrous on the fractured surface; extremely difficult to pulverize when quite dry, but easily rubbed to a soft powder after partial drying. When recently washed and still moist, it reddens litmus paper. After drying in the air, it still loses water when heated. (Erdmann.)

	Lose. (1).	Erdmann. (2 *a*).	(2 *b*).	*Approximate Calculation.*		
C	62·76	67·72	68·47	28 C	168	67·74
H	4·01	3·33	2·26	8 H	8	3·23
O	27·00	22·40		7 O	56	22·58
S	6·23	6·55		S	16	6·45
	100·00	100·00		$C^{28}H^8O^4,SO^3$?	248	100·00

Erdmann's preparations were dried at 150°; he gives the preference to the formula $C^{80}H^{24}O^{20}S^3$; Lose, from his own analysis, which differs greatly from Erdmann's, deduces the formula $C^{27}H^{10\cdot5}O^9S = C^{27}H^{4\cdot5},6HO,SO^3$.

Decompositions. Thiomelanic acid yields, by dry distillation, sulphide of carbon, sulphur, and a small quantity of sulphuretted hydrogen (Bischof); water, carbonic acid, sulphurous acid, sulphuretted hydrogen, sulphur, and a brown oil. (Marchand and Erdmann.) Lose obtained the

same products with the exception of the oil. — It is extremely difficult to burn, and when ignited in the air for several hours over the flame of a spirit-lamp, still leaves a carbonaceous residue which burns away completely when moistened with nitric acid. It is completely decomposed by continued boiling with nitric acid. When heated with hydrate of potash, it swells up, gives off a combustible gas, and leaves a fused white mixture of sulphate of potash and sulphide of potassium. It is not decomposed, either by other acids, such as nitric acid, at a boiling heat, or by boiling caustic alkalis. (Lose.)

Combinations. The acid does not dissolve either in water or in alkalis, but when digested in aqueous solutions of the alkalis or of sugar of lead, it takes up a certain quantity of base, and forms an insoluble salt externally resembling the acid itself. (Erdmann.)

The *Ammonia-salt* is obtained: (*a*) by digesting the acid prepared by (2) with ammonia of definite strength. — The following modes of preparation, on the other hand, yield a salt of variable composition, probably because the alcohol, not being heated long enough or strongly enough with the oil of vitriol, small quantities of other compounds remain mixed with the product. — *b.* By treating the salt prepared by (1) with ammonia. — *c.* By heating 1 pt. of alcohol of sp. gr. 0·83 with 6 pts. of fuming oil of vitriol in a retort, till the gas which is evolved ceases to be combustible, washing the residue repeatedly with water, then boiling it with dilute ammonia, and washing it with boiling water, till the liquid which runs through no longer forms a cloud with chloride of barium. — *d.* The same as *c*, excepting that rectified oil of vitriol is used instead of the fuming acid. — The compound when treated with aqueous potash, gives off ammonia abundantly, and is converted into the potash-salt. (Erdmann.)

Erdmann (*the salt being dried at* 150°).

	(*a*).			
C	64·3	64·30	66·11	65·58
H	3·8	3·33	3·78	4·55
O + N		24·88	21·19	21·49
S		7·49	8·92	8·38
		100·00	100·00	100·00

Potash-salt. — Obtained by boiling the acid prepared by (2) and still moist, with caustic potash, and washing the mass with boiling water, till the water no longer acquires any alkaline reaction. A small quantity of the salt in a soft and finely divided state diffuses through the water and gives it a brownish tint, but it is deposited on saturating the solution with common salt. (Erdmann.)

Erdmann (*the salt dried at* 150°; *mean*).

KO	11·35
C	59·78
H	2·91
O	20·26
S	5·70
	100·00

Baryta-salt.—Thiomelanic acid boiled with aqueous chloride of barium, gives off hydrochloric acid, and after washing, yields a baryta-salt which is free from chlorine, and when burnt, leaves 16·61 per cent. of sulphate of baryta. (Erdmann.)

Lead-salt. — Prepared by boiling the acid with aqueous acetate of lead, whereupon acetic acid is given off, and washing the product. The compound is free from acetic acid, and when burnt after drying, leaves 31·13 per cent. of sulphate of lead. (Erdmann.)

The analyses of these salts do not agree very well among themselves, probably because, from the insolubility of the acid, the bases combine with it but imperfectly. (Gm.)

14. *Phosphoric acid* acts upon alcohol, to a certain extent, like sulphuric acid,—that is to say, it forms a phosphovinic acid analogous to sulphovinic acid, and by its water-forming power, gives rise to the production of ether, olefiant gas, and a kind of wine-oil; but it does not exhibit any oxidating power.

100 pts. of highly concentrated phosphoric acid (which, dissolved in water and precipitated by excess of baryta-water, would yield 218 pts. of phosphate of baryta), dissolved in 100 pts. of 95 per cent. alcohol and set aside for 24 hours in a vessel surrounded with ice, yield 150 pts. of phosphate of baryta, and after boiling for a short time, 148 pts. — Hence the quantity of phosphoric acid converted into phosphovinic acid amounts to about $\frac{1}{4}$ of the acid used, and the product is not much larger when heat is applied. (Pelouze, *J. Chim. méd.* 9, 141; vid. *Phosphovinic acid.*)

Anhydrous phosphoric acid (prepared by burning phosphorus in dry oxygen) dissolved in a small quantity of absolute alcohol, gives out great heat, and yields a syrup which, when heated, does not give off ether, but only olefiant gas. — But if the alcohol is in excess, the mixture begins to boil at 80°, yields alcohol till the temperature rises to 140°, and then ceases to boil till it reaches 175°, at which temperature a small quantity of ether passes over at first, and then, between 175° and 200°, olefiant gas and a small quantity of a thickish acid distillate which does not precipitate baryta-water. The residue remains colourless during the whole process. (Kuhlmann, *Ann. Pharm.* 33, 217.)

Alcohol, when distilled even with large quantities of [hydrated?] phosphoric acid, yields but a small quantity of ether, not containing either wine-oil or the phosphovinate of wine-oil. The residue chars, and yields olefiant gas, water, together with a small quantity of an oil which floats on the water and has an odour different from that of wine-oil. (Serullas, *Ann. Chim. Phys.* 39, 152; also *Schw.* 55, 170.)

Respecting etherification by phosphoric acid, according to Boullay, *vid.* p. 174.

Aqueous phosphoric acid of sp. gr. less than 1·2 has no action upon alcohol; but 5 pts. of the syrupy acid heated with 1 pt. alcohol yield, with brisk effervescence, a large quantity of olefiant gas, and a small quantity of wine-oil, the mixture assuming a deep brown colour, and depositing light carbonaceous flakes. Phosphoric acid forms ether much less quickly than sulphuric acid, not because it unites less readily with the alcohol, but because the phosphovinic acid formed in the process resists decomposition much more strongly than sulphovinic acid. (Pelouze, *J. Chim. méd.* 9, 131 and 145.)

At the commencement of the distillation, the dilute phosphoric acid formed together with the phosphovinic acid, gives off its water; the phosphovinic acid is then resolved into hydrated phosphoric acid, which gives off no more water, even when more strongly heated, and ether, which in the end is partly resolved into wine-oil and alcohol [water?] (Liebig, *Handwörterb.* 1, 115.)

15. When 3 pts. of vitrefied boracic acid in the state of powder are heated with 1 pt. of absolute alcohol, olefiant gas is given off abundantly and regularly; the mixture does not blacken, but leaves a residue of mono-hydrated boracic acid, which does not give off water till more strongly heated. (Ebelmen, *Compt. rend.* 18, 1203; vid. also *Boracic ether.*)

16. *Arsenic acid* acts very much like phosphoric acid, producing both arseniovinic acid and ether (p. 175). The observations of Liebig just quoted respecting phosphoric acid, apply also, according to his statement, to arsenic acid.

17. *Chromic acid* exerts a violent oxidizing action upon alcohol, the acid being reduced to chromic oxide, the alcohol sometimes taking fire, and when that effect does not take place, being converted into aldehyde, acetic acid, and acetic ether.

If a teaspoonful of dry chromic acid be introduced into a porcelain capsule wetted with absolute alcohol, the alcohol instantly takes fire, and the resulting chromic oxide continues to glow for some time, giving off a powerful odour of aldehyde. The alcohol takes fire still more readily, if a small quantity of sulphide of carbon be mixed with it, although that compound by itself exerts but little action on chromic acid. — If alcohol be suffered to evaporate in a bottle filled with air, and a small quantity of chromic acid dropped in, the mixture explodes. If a little alcohol be again allowed to evaporate in the bottle, and a small quantity of chromic acid then introduced, it will be seen, if the room be rather dark, to run about in the glass for 6 or 10 minutes in a finely divided state and red-hot. (Böttger, *Ann. Pharm.* 37, 117.)

If a glow-lamp having an asbestus wick be filled with 80 per cent. alcohol, the wick cut off about $\frac{1}{4}$ of an inch above the mouth, somewhat spread out, its upper part moistened with a few drops of absolute alcohol, and as much crystallized anhydrous chromic acid as can be placed on the point of a knife sprinkled upon it, the alcohol immediately takes fire, and brings the chromic oxide derived from the decomposition of the chromic acid to bright redness. If the flame be then blown out, the chromic oxide continues to glow still more strongly, till all the alcohol in the lamp is consumed, yielding a kind of lampic acid containing aldehyde. — If the alcohol contains bisulphide of carbon, a liquid smelling of mercaptan is produced. (Böttger, *Ann. Pharm.* 57, 134.)

When chromic acid is dissolved in absolute alcohol, heat is evolved, and an odour of nitrous ether (aldehyde) produced; at a somewhat higher temperature, the mixture boils, part of the chromic acid being then reduced to brown oxide. (Meissner, *Gilb.* 60, 372.) — When chromic acid is boiled with alcohol, an ether is formed resembling Döbereiner's oxygen-ether (aldehyde), and there remains a dark-brown liquid containing brown oxide of chromium. (Unverdorben, *N. Tr.* 9, 1, 31.)

A mixture of concentrated sulphuric acid and chromic acid produces with alcohol a degree of heat amounting to explosion, and yields ether and wine-oil, perhaps also acetic ether, while chromic sulphate remains behind. (Gay-Lussac, *Ann. Chim. Phys.* 16, 102.) — Chromic acid containing sulphuric acid behaves with alcohol in the same manner as oxide of manganese mixed with sulphuric acid. (Döbereiner.) — Sulphuric acid with chromate of potash converts alcohol into acetic acid and acetic ether. (Duflos, *Kastn. Arch.* 14, 309.) Mitscherlich (*Pogg.* 14, 538,) also obtained acetic ether. — Alcohol brought in contact with chromic acid,

or with a mixture of sulphuric acid and chromate of potash, becomes heated, so that no external heat is necessary till towards the end of the action, and forms aldehyde, acetic acid, carbonic acid, and perhaps also formic acid. When the alcohol is added in small portions to the mixture of chromate of potash and sulphuric acid, acetic acid is the chief product formed, but if the process be reversed, aldehyde is the principal product. (W. & R. Rogers, *Chem. Gaz.* 1846, No. 92, 322; also *J. pr. Chem.* 40, 240.)

When a heated mixture of alcohol and oil of vitriol is poured into a concentrated solution of chromate of potash, a dark green, oily mass is formed, which is not soluble in alcohol, but forms a *green ink* with water, and a green varnish with oil-varnish (Leykauf, *J. pr. Chem.* 19, 125.) [sulphovinate of chromic oxide ?]

18. Alcohol mixed with *Black Oxide of Manganese* and *Sulphuric acid* becomes heated, and produces ether, aldehyde, acetic acid, acetic ether, formic acid, formic ether, carbonic acid, and sulphovinate of wine-oil, the manganese being converted into manganous sulphate.

2 pts. of alcohol with 1 pt. sulphuric acid and 2 pts. manganese yield ether having an agreeable odour, together with acetic and carbonic acid. (Scheele, *comp.* also Laudet & Dabit, *Scher. J.* 6, 440 and 447.) — Alcohol mixed with oil of vitriol in presence of manganese, forms a liquid differing in its properties from alcohol and ether, and miscible with water. (Fourcroy & Vauquelin.) — Ether and wine-oil are produced in this reaction, perhaps also acetic acid, while the residue contains no sulphovinic acid, but only manganous sulphate. (Gay-Lussac, *Ann. Chim. Phys.* 16, 102; also *Schw.* 32, 448.)

46 pts. of absolute alcohol mixed in a retort with 123 pts. oil of vitriol and 135 pts. manganese, become strongly heated, and when distilled into a well cooled receiver, yield in a few minutes a distillate which separates into two layers, the upper of which consists of water, alcohol, acetic acid, and a small quantity of oxygen-ether [aldehyde], and the lower, which is oily (and was for a while called *heavy oxygen-ether*), of sulphovinate of wine-oil and oxygen-ether [aldehyde], converted into a resin when heated with potash. (Döbereiner, *Schw.* 32, 269; 31, 124; 38, 327; 63, 366.) — The oily distillate obtained by Döbereiner is, in fact, sulphovinate of wine-oil; the upper layer contains ether and a volatile substance [aldehyde], which has an unpleasant odour, and is converted into a resin by potash. (Liebig, *Pogg.* 24, 246.) — When the materials are mixed in the proportions used by Döbereiner (46 : 123 : 135), no oil of wine is obtained, unless the application of heat be continued from without after the ebullition produced by the first gentle heat has subsided, the products of this first stage of the action being water, alcohol, acetic acid, acetic ether, and oxygen-ether. (Duflos, *Berl. Jahrb.* 27, 1, 84.) — According to Dumas & Boullay (*J. Pharm.* 14, 11; also *Schw.* 52, 67); oil of wine passes over, together with ether, during the whole of the process, inasmuch as it cannot be retained by the sulphuric acid which combines with the manganous oxide; the addition of manganese is unfavourable to the formation of ether.

When dilute alcohol is distilled with manganese and sulphuric acid, a large quantity of formic acid is obtained, in addition to the acetic acid (less if strong alcohol be used), also formic ether. (C. G. Gmelin, *Pogg.* 16, 55.) This observation has been confirmed by Connell (*N. Edinb. J.* 14, 240), and by Gm. (*Pogg.* 28, 508.) — A mixture of 2 pts. 80 per cent. alcohol, 3 pts. manganese, 3 pts. oil of vitriol, and 2 pts. water

froths up when moderately heated, at first giving off chiefly aldehyde, together with undecomposed alcohol, and a quantity of carbonic acid so small that it remains dissolved in the distillate, then principally acetic and formic ether, and finally acetic and formic acid. The distillate also contains traces of ether; but no acetal can be detected in it. (Liebig, *Ann. Pharm.* 134, 135 and 151.)

19. *Uranic sulphate* dissolved in hydrated alcohol and exposed to sunshine, is reduced to uranous sulphate, and yields aldehyde. (Ebelmen, *N. Ann. Chim. Phys.* 5, 205.)

20. *Vanadic acid* is reduced by alcohol to vanadic oxide. (Berzelius.)

21. From a solution of *Osmic acid* in alcohol, the reduced metal separates in 24 hours.

22. Alcohol mixed with aqueous *Bichloride of Platinum* and excess of potash, and exposed to the heat of the sun, yields platinum-black and acetate of potash; if the platinum-solution contains nitric acid, a large quantity of ammonia is likewise given off. (Döbereiner, *Ann. Pharm.* 2, 1;—*Schw.* 63, 476.)

23. A saturated solution of corrosive sublimate in alcohol, mixed with a quantity of pounded lime equal in weight to the sublimate,—whereby all the mercury is converted into *Mercuric oxide*,—becomes heated, gives off a faint ethereal odour, assumes a red-brown colour, and is converted into a creamy liquid, which is yellowish brown at first, but afterwards becomes grey, from the presence of reduced mercury; this liquid when distilled yields acetic ether, a proof that acetic acid has been previously formed. (Duflos, *Berl. Jahrb.* 27, 1, 76.)

24. Anhydrous *Hydrofluoric acid* appears to convert alcohol into hydrofluoric ether. (Reinsch.)

25. Alcohol saturated with *Fluoboric gas* is resolved by heat into ether and hydrofluate of boracic acid (Desfosses):

$$3C^4H^6O^2 + BF^3 = 3C^4H^5O + BO^3,3HF^3.$$

Alcohol of 42° Bm. saturated with fluoboric gas becomes turbid after a while, and deposits a small quantity of carbonaceous powder; when distilled, it yields nothing but ether (no oil of wine), and at last a small quantity of carbonic acid and carburetted hydrogen gas, while hydrofluate of boracic acid remains behind. (Desfosses, *Ann. Chim. Phys.* 16, 72.)

Absolute alcohol absorbs fluoboric gas, becoming heated thereby. The colourless, sour-smelling mixture, which fumes in the air, is resolved on addition of water into alcohol and hydrofluate of boracic acid. If, on the other hand, it be distilled, it begins to boil at 80°, and between 80° and 135°, yields a colourless distillate, which burns with a green flame, a strong white fume, and a black-brown residue; this distillate is merely a compound of alcohol and fluoride of boron, contaminated with a small quantity of fluoride of silicium. Between 135° and 170°, a mixture of ether and fluoride of boron passes over, which burns with a green flame and a white smoke, gives off an odour of ether when mixed with water, but does not yield a layer of ether till potash is added. Above 170°, a thickish distillate is obtained, which appears to be formed by the decomposition of ether. In the retort there remains a small quantity of an acid

substance which dissolves in water, leaving a jelly of silica. — If the distillation be interrupted as soon as the boiling point has risen to 155°, and the residue be then mixed with caustic potash, it becomes strongly heated, evolving ether, and when distilled yields, first ether and then alcohol. Hence the residue contains an ether-compound; the alcohol either occurs as such in the residue, or is reproduced from the ether-compound by the water of the potash-solution. — When absolute alcohol saturated with fluoboric gas is left for 14 days in a close vessel at a temperature of 12° or 15°, the mixture is found not to have altered in appearance, but on addition of water gives off an alliaceous odour and yields a yellow oil. The watery mixture when distilled first gives off a large quantity of alcohol having a disagreeable odour, apparently due to the yellow oil which separates out partially as the liquid cools. From the reddish brown residue, on the surface of which a few drops of oil float, a compound of boracic acid with oil separates on cooling, in rose-coloured nodules, which when distilled turn black, yield oil, and then melt; this compound dissolves sparingly in cold water and is decomposed by potash. The only product here formed is therefore the oil; the formation of ether appears to take place only between 140° and 160°. (Kuhlmann, *Ann. Pharm.* 33, 205 and 233.)

26. Alcohol saturated as completely as possible with *Fluosilicic acid gas* by passing the gas through it for 16 hours, fumes very strongly, thickens by formation of gelatinous silica, and if afterwards distilled yields common ether. (R. F. Marchand, *J. pr. Chem.* 13, 499.)—Liebig & Wöhler (*Pogg.* 24, 172) did not succeed in the attempt to form ether by means of fluoride of silicium.

27. The yellow solution of *Terfluoride of Chromium* in absolute alcohol soon emits an odour of chloride of ethyl, and deposits a dark green thickish liquid consisting of acid hydrofluate of chromic oxide, the supernatant liquid not retaining any fluorine. (Unverdorben.) — Absolute alcohol absorbs the vapour of terfluoride of chromium, with great evolution of heat, the bubbles as they enter often producing a white flame. The liquid deposits a large quantity of brownish green powder, and acquires the odour of heavy hydrochloric ether. But no ethereal liquid separates on the addition of water, even when the alcohol is so strongly charged with fluoride of chromium as to emit fumes. (Wöhler, *Pogg.* 13, 299.)

28. *Fluoride of Arsenic* mixes with alcohol, causing slight evolution of heat and forming a small quantity of ethereal liquid.

29. Strong *Hydrochloric acid* mixed with alcohol forms chloride of ethyl. (*q. v.*)

30. *Terchloride of Phosphorus* poured into alcohol of 36° Bm. acts violently on it, producing hydrochloric acid, chloride of ethyl, phosphosovinic acid, and a small quantity of phosphorous acid. (Wurtz, *Compt. rend.* 21, 357.) — *Chloride of Boron* forms a boracic ether. (*q. v.*)

31. *Protochloride of Sulphur* and alcohol mixed together, effervesce strongly and produce hydrochloric ether and sulphurous acid. (Thomson.)

32. When *Chlorosulphuric acid*, $SClO^2$, is dropped into alcohol, every drop makes a hissing noise like red-hot iron plunged in water, emitting

at the same time a pungent odour like that of hydrochloric ether, and forming a large quantity of sulphovinic acid. (Regnault.)

33. The colourless, viscid solution of *Chloride of Aluminum* in absolute alcohol, the formation of which is attended with great evolution of heat, first yields by distillation, alcohol containing in solution a small quantity of chloride of aluminum, and having a repulsive alliaceous odour; becomes somewhat coloured at 170°; gives off hydrochloric ether between 170° and 200°, and afterwards a large quantity of hydrochloric acid; the residue contains a large quantity of alumina. (Kuhlmann, *Ann. Pharm.* 33, 204.) — *Chloride of Silicium* forms various silicic ethers. (*q. v.*)

34. *Chlorochromic acid*, $CrClO^2$, in contact with absolute alcohol produces heat sufficient almost to set the alcohol on fire; the mixture gives off heavy hydrochloric ether and forms a green solution of sesquichloride of chromium. (Wöhler, *Pogg.* 13, 298.) — Thomson (*Pogg.* 31, 607) also noticed the inflammation. — According to Walter (*Ann. Chim. Phys.* 66, 389, the action is sometimes strong enough to scatter the alcohol about with violent explosion.

35. The red solution of *Terchloride of Vanadium* in absolute alcohol changes first to green, then to blue, with formation of hydrochloric ether. (Berzelius.)

A mixture of *Chloride of Arsenic* and absolute alcohol does not yield any ethereal liquid by distillation, but between 115° and 130° it gives off unaltered alcohol; the boiling then ceases, but begins again at 180°, at which temperature, pure chloride of arsenic passes over. (Kuhlmann, *Ann. Pharm.* 33, 204.)

36. Absolute alcohol mixes with *Pentachloride of Antimony*, assuming a green colour and producing great heat. If the mixture contains excess of alcohol, it yields by distillation between 140° and 170°, hydrochloric ether apparently mixed with common ether; above 170°, a large quantity of hydrochloric acid is evolved, and the residue consists chiefly of powder of algaroth. — If the mixture contains excess of pentachloride of antimony, the formation of hydrochloric ether begins at 85°. — If the mixture be set aside for some hours, a brown oil separates from it on the addition of water. (Kuhlmann, *Ann. Pharm.* 33, 106 and 203.) — Hydrochloric ether is likewise obtained on distilling alcohol with *Terchloride of Antimony.* (*q. v.*)

37. The alcoholic solution of corrosive sublimate deposits calomel very slowly. (VI. 58.)

38. *Protochloride of Platinum* scarcely acts on alcohol of sp. gr. 0·813 to 0·893 when only moderately heated; but on boiling, the grey-green powder turns black, and the almost colourless liquid acquires a strongly acid reaction and the odour of hydrochloric ether. (Zeise, *Pogg.* 9, 632; 21, 498.) [The black powder thus produced (described, VI, *c*, *β*) and distinguished by the combustion and hissing noise which it exhibits when heated, appears to be $C^4H^4Pt^2O^2$; it will be more fully described further on, under the title of *Detonating Platinum-Deposit.* According to this formula, the equation for its formation must be:

$$C^4H^6O^2 + 2PtCl = C^4H^4Pt^2O^2 + 2HCl;$$

the hydrochloric acid thus produced converts another portion of the alcohol into hydrochloric acid.]

If the protochloride of platinum contains any bichloride, it immediately evolves with alcohol the odour of hydrochloric ether, and changes in three or four days, even at ordinary temperatures, into the black powder; the supernatant brown liquid deposits more of this powder when distilled.

39. The solution of 1 pt. *Bichloride of Platinum* in 10 pts. alcohol, of sp. gr. 0·823, distilled to $\frac{1}{6}$, yields alcohol, aldehyde, hydrochloric ether and hydrochloric acid. The residual dark brown liquid still has a faint ethereal odour, contains a large quantity of free hydrochloric acid, deposits a considerable quantity of the black powder (detonating platinum-deposit), and contains in solution inflammable chloride of platinum, which no longer forms a precipitate with sal-ammoniac. (Zeise, *Pogg.* 21, 498; 40, 240.)

Equation, according to Zeise (inflammable chloride of platinum being supposed $= C^4H^4Pt^2Cl^2$):

$$2C^4H^6O^2 + 2PtCl^2 = C^4H^4Pt^2Cl^2 + C^4H^4O^2 + 2HO + 2HCl.$$

Part of the hydrochloric acid thus produced forms hydrochloric ether with the rest of the alcohol. — According to Liebig, who considers inflammable chloride of platinum as $C^4H^3Pt^2Cl^2$, the equation is:

$$3C^4H^6O^2 + 4PtCl^2 = 2C^4H^3Pt^2Cl^2 + C^4H^4O^2 + 4HO + 4HCl.$$

The formation of the detonating platinum deposit is not an essential feature of this reaction, the quantity of the detonating compound formed being in fact less, in proportion as the bichloride of platinum is more free from protochloride, which latter compound, according to the preceding, forms with alcohol the detonating platinum deposit. If the aqueous solution of bichloride of platinum be ultimately evaporated in vacuo over hydrate of potash, and then dissolved in the quantity of alcohol just sufficient to convert it into inflammable chloride of platinum, the quantity of bichloride converted into the black deposit does not exceed $\frac{1}{100}$ of the whole. If an excess of alcohol be used, and the distillation be continued till the residue becomes highly concentrated, a larger quantity is formed, because the inflammable chloride of platinum produced at the beginning of the action is decomposed by the alcohol. Moreover, if the aqueous platinum solution be concentrated by heat till it no longer gives off hydrochloric acid, a certain quantity of protochloride of platinum is formed, and dissolves in the alcohol through the medium of the remaining bichloride; in that case, from $\frac{1}{4}$ to $\frac{1}{3}$ of the evaporated residue is converted into the black deposit. The formation of this compound is due, therefore, partly to the excess of alcohol, partly to the protochloride of platinum (Zeise.) — Generally speaking, 10 pts. of alcohol are sufficient to convert 1 pt. of bichloride of platinum into the inflammable chloride; but sometimes the same quantity of bichloride must be boiled with 3 or 4 times the quantity of alcohol, to ensure that the residual liquid shall be free from bichloride, and consequently shall no longer yield a precipitate with sal-ammoniac; in this case, the reaction is sometimes accelerated by addition of water. (Zeise.) — [This transformation appears to take place even at ordinary temperatures; for the alcoholic solution of bichloride of platinum sometimes prepared as a test for potash and ammonia-salts, gradually loses the power of precipitating them.]

The brown liquid separated from the black platinum-deposit, if carefully evaporated to dryness and treated with cold water, gives up the

inflammable chloride to the water, and leaves more or less of a brown mucous mass, having a peculiar odour. This substance, even when thoroughly washed, contains carbon, hydrogen, and platinum; gives off hydrochloric acid and leaves platinum when heated; and dissolves in aqua-regia, leaving a brownish resinous substance which, when heated, swells up strongly, takes fire and burns away quickly with a glimmering light, leaving spongy platinum. The quantity of this brown mucous mass is less, the more dilute the alcohol and the less the distillation is carried out; it is probably formed by decomposition of the inflammable chloride of platinum. (Zeise.)

40. Alcohol heated with *Sesquichloride of Iron* is chiefly converted into chloride of ethyl, hydrochloric acid, water, and ferric oxide, a small portion, however, being resolved into ether and water. (Kuhlmann.)

Equation for the formation of the chloride of ethyl:

$$2C^4H^6O^2 + Fe^2Cl^3 = 2C^4H^5Cl + HCl + HO + Fe^2O^3;$$

or, according to Kuhlmann;

$$3C^4H^6O^2 + 2Fe^2Cl^3 = 3C^4H^5Cl + 3HCl + 2Fe^2O^3;$$

For the formation of ether, which takes place only when at least 2 At. alcohol are brought in contact with 1 At. sesquichloride of iron:

$$C^4H^6O^2 + xFe^2Cl^3 = C^4H^5O + HO,xFe^2Cl^3;$$

or, according to Kuhlmann, who supposes that, in this case, ether and chloride of ethyl are formed by one and the same process;

$$4C^4H^6O^2 + 2Fe^2Cl^3 = 3C^4H^5Cl + C^4H^5O + HO + 3HCl + 2Fe^2O^3.$$

A mixture of 100 pts. (1 At.) sesquichloride of iron and 28·91 pts. (1 At.) absolute alcohol begins to froth up at 90°; from that temperature to 150°, yields a large quantity of chloride of ethyl with but little hydrochloric acid; from 150° to 170°, a small quantity of chloride of ethyl and a large quantity of hydrochloric acid; and above 180°, nothing but hydrochloric acid in large quantity. In this case, 100 measures of alcohol yield 73 measures of hydrochloric ether. (Kuhlmann.)

100 pts. (1 At.) Fe^2Cl^3 with 57·32 pts. (2 At.) alcohol begin to froth up slightly at 120°, and at 130° yield chloride of ethyl with a small quantity of ether; between 140° and 150°, the same products together with sesquichloride of iron; at 155°, at which temperature the mass thickens, and at 160° when it becomes dry, the chief product is hydrochloric acid; and at 170°, nothing but hydrochloric acid and water are evolved. The residue consists of sesquioxide and sesquichloride of iron. 100 vol. alcohol thus treated yield 97 vol. chloride of ethyl mixed with common ether.

100 pts. (1 At.) sesquichloride of iron and 115·63 pts. (4 At.) alcohol begin to froth up at 75°; yield pure alcohol from that temperature to 145°; between 145° and 160°, chloride of ethyl mixed with ether; at 165°, hydrochloric acid, the residue thickening at the same time; at 170°, hydrochloric acid with small quantities of water and chloride of ethyl; at 180°, hydrochloric acid, water, and a small quantity of sesquichloride of iron. The alcohol which passes over undecomposed amounts to 58·54 pts., therefore to half the quantity used, and 100 vol. of alcohol decomposed yield 85 vol. chloride of ethyl containing ether. (Kuhlmann.)

When alcohol is distilled with hydrated sesquichloride of iron, the

excess of alcohol passes over first, then at 140°, chloride of ethyl mixed with ether (the quantity of ether being greater than when water is absent); then follows a small quantity of sweet oil of wine, and lastly, a considerable quantity of hydrochloric acid mixed with water. — When dry sesquichloride of iron is distilled with absolute alcohol under a pressure reduced to 4 centimetres of mercury, alcohol passes over first, then hydrochloric acid and water; but no chloride of ethyl is obtained, even when the receiver is cooled down to — 10°. (Kuhlmann. *Ann. Pharm.* 33, 106 and 200.)

A solution of 1 pt. sesquichloride of iron in 4 pts. alcohol changes colour in sunshine more quickly than the ethereal solution; it does not become colourless, but assumes a light blue tint, and deposits nothing but a trace of black powder. If then distilled, it yields a liquid which smells of heavy hydrochloric ether and contains free hydrochloric acid; the residue consists of protochloride of iron without any admixture of resin. (Kerner, *Ann. Pharm.* 29, 68.) — The solution decolorized by light, becomes brown again on exposure to the air. (Grotthuss.)

41. Dry *Protochloride of Iron* decomposes absolute alchohol into ether and water, even at a moderate heat. The solution placed in a well closed vessel and set aside for some months in a moderately warm place, deposits hydrated protochloride of iron in the form of a white radiated mass, and the supernatant alcohol holds in solution a considerable quantity of ether. (Döbereiner, *Gilb.* 68, 88.) [This is the only case of etherification at so low a temperature.]

42. *Bichloride of Tin* acts upon alcohol much in the same manner as sesquichloride of iron, producing chloride of ethyl, common ether, hydrochloric acid, and binoxide of tin. When the bichloride of tin is in excess, it forms with the resulting ether and chloride of ethyl, a thick, heavy, oily, crystallizable compound, which distils over; water added to the distillate causes the chloride of ethyl and the ether to separate out. (Kuhlmann.)

Formation of chloride of ethyl:

$$2C^4H^6O^2 + SnCl^2 = 2C^4H^5Cl + 2HO + SnO^2;$$

of ether:

$$2C^4H^6O^2 + SnCl^2 = 2C^4H^5O + SnCl^2,2HO\ ?$$

Kuhlmann supposes that a peculiar compound of bichloride of tin with the binoxide remains behind; accordingly, he writes the first equation in the following manner:

$$2C^4H^6O^2 + 2SnCl^2 = 2C^4H^5Cl + 2HO + SnCl^2,SnO^2.$$

Instead of the second equation, Kuhlmann gives two, which express the formation of chloride of ethyl and common ether at the same time, viz.:

$$3C^4H^6O^2 + 2SnCl^2 = 2C^4H^5Cl + C^4H^5O + 3HO + SnCl^2,SnO^2;$$

and:

$$3C^4H^6O^2 + 2SnCl^2 = C^4H^5Cl + 2C^4H^5O + 3HCl + 2SnO^2.$$

Gerhardt (*Rev. scient.* 19, 304) supposes that only hydrochloric ether is at first produced:

$$2C^4H^6O^2 + SnCl^2 = 2C^4H^5O + SnO^2 + 2HCl,$$

and that the hydrochloric acid thus formed converts another portion of the alcohol into hydrochloric ether.

100 pts. (2 At.) of bichloride of tin and 17·93 pts. (1 At.) of absolute alcohol distilled together, yield bichloride of tin without effervescence between 100° and 120°; at 140°, the mixture boils and yields bichloride of tin together with hydrochloric acid; at 150°, bichloride of tin, the total quantity of that compound distilled over at this and the lower temperatures together, amounting to $\frac{1}{3}$ of the whole; at 160°, a viscid compound of bichloride of tin and chloride of ethyl; at 170°, the same compound, but in two layers, the upper containing more chloride of ethyl than the lower: between 180° and 200°, a small quantity of viscid liquid is obtained, together with an oil which sinks to the bottom. When water is added to the distillates consisting of bichloride of tin and chloride of ethyl, heat is developed sufficient to drive off the chloride of ethyl with violent ebullition. With the above proportion, no ether is formed. (Kuhlmann.)

100 pts. (10 At.) of bichloride of tin and 32·84 pts. (9 At.) absolute alcohol yield between 140° and 150° a small quantity of chloride of ethyl unmixed with ether; the residue crystallizes on cooling in silky heaps, and does not yield any stratum of ether on the addition of water. The mixture when distilled after this addition of water, boils at 80°, yields at 170°, nothing but water and alcohol, and above 170°, becomes thick, yielding a large quantity of binoxide of tin. Hence the water appears to have reproduced the alcohol. (Kuhlmann.)

100 pts. (1 At.) bichloride of tin and 35·87 pts. (1 At.) alcohol give off at 127° a small quantity of chloride of ethyl and hydrochloric acid; at 135°, a larger quantity, with slight intumescence; at 150°, a large quantity of chloride of ethyl, with a little ether and very little hydrochloric acid, the liquid boiling regularly; at 155°, chloride of ethyl and ether, generally united with chloride of tin in the form of a colourless, heavy, viscid oil, which crystallizes in stellate groups on cooling, mixes with ether, and contains hydrochloric acid: between 160° and 200°, an additional quantity of this viscid oil passes over, becoming yellowish at the last. The residue, amounting to 28 pts, still contains a small quantity of this oily compound, besides protochloride of tin. If to the oily compound which has passed over, there be gradually added an equal measure of potash-ley, chloride of ethyl evaporates and a layer of common ether rises to the surface. In this distillation, 100 vol. alcohol yield 46 vol. chloride of ethyl mixed with ether. (Kuhlmann.)

100 pts. (3 At.) bichloride of tin and 44·5 pts. (about 4 At.) of absolute alcohol yield, at 120°, a small quantity of hydrochloric acid; between 145° and 160°, chloride of ethyl and hydrochloric acid; at 180°, chloride of ethyl and ether, combined with bichloride of tin. 100 vol. alcohol thus decomposed yield 41 vol. chloride of ethyl containing ether. (Kuhlmann.)

100 vol. (2 At.) bichloride of tin, and 46·25 pts. absolute alcohol, begin to boil at 130°; yield between 140° and 165° chloride of ethyl and ether, with a very small quantity of alcohol; then, at 170°, the same products, united with bichloride of tin into a syrup; and, between 175° and 200°, the same syrup, together with hydrochloric acid and water. In this case, 100 vol. alcohol yield 57 vol. of a mixture of chloride of ethyl in ether, which is the maximum product. (Kuhlmann.)

100 pts. (1 At.) bichloride of tin and 71·74 pts. (2 At.) absolute alcohol yield absolute alcohol between 120° and 140°; at 150°, alcohol with traces of chloride of ethyl and ether; at 160°, when the residue contains about 3 At. alcohol and 2 At. bichloride of tin, chloride of ethyl

and ether pass over; at 170°, chiefly the former; at 180°, hydrochloric acid; at 185°, the oily mixture of chloride of ethyl and bichloride of tin, separable by water. The residue contains a large quantity of binoxide of tin. 100 vol. of alcohol thus decomposed yield 48 vol. chloride of ethyl. (Kuhlmann.)

If hydrated alcohol be used, alcohol passes over first; then, at 150° chloride of ethyl and ether, together with water. (Kuhlmann, *Ann. Pharm.* 33, 106 and 192.)

When equal measures of bichloride of tin and absolute alcohol are distilled together, in an apparatus exhausted down to a pressure of 4 cub. cent. of mercury, and having a receiver surrounded with a frigorific mixture, a small quantity of the compound of bichloride of tin with alcohol sublimes into the neck of the retort; then from 60°, at which temperature the mass melts, to 100°, bichloride of tin with a small quantity of hydrochloric acid and alcohol distils over in the form of a rose-coloured liquid. If the fuming residue be now mixed with half as much alcohol as was at first used, and the air again pumped out, nearly all the recently added alcohol passes over with ebullition at 85°; then at 95°, also a small quantity of the compound of alcohol with bichloride of tin; then, at 125°, bichloride of tin together with hydrochloric acid. The distillate yields no oil when mixed with water, and contains at the utmost mere traces of hydrochloric ether. The residue in the retort, after the heat has been raised to 160°, is white and light, and, when further heated, swells up, chars, gives off empyreumatic oil, and is partly converted into protochloride of tin. Hence when the atmospheric pressure is removed, only a trace of hydrochloric ether is formed, and no oil (as with oil of vitriol, pp. 231, 232.) The oil is probably retained by the residue. (Kuhlmann, *Ann. Pharm.* 33, 221.)

According to former experiments by Duflos, absolute alcohol becomes strongly heated with bichloride of tin, and emits an odour of ether; but, when further heated, gives off hydrochloric ether.

43. *Protochloride of Tin* distilled with alcohol produces ether but no chloride of ethyl; the mass is very apt to froth over. (R. F. Marchand, *J. pr. Chem.* 13, 499.)

44. Alcohol heated with *Chloride of Zinc* produces ether and oil of wine, and, under certain circumstances, also olefiant gas and chloride of ethyl.

Alcohol of 36° Bm. saturated with chloride of zinc *not quite anhydrous*, and distilled, gave in three experiments the following results:

Exp. 1. At 71°, alcohol; at 90°, the mixture boils and yields alcohol of 92 per cent; between 95° and 140°, alcohol of 93 p.c; at 108°, alcohol of 92 p.c; at 120°, alcohol of 91 p.c; at 130°, alcohol of 90 p.c; from 150° to 162°, alcohol with a large quantity of ether; at 182°, alcohol, ether, and a large quantity of water; at 200°, wine-oil and water; at 220°, the mixture swells up strongly; at 250°, nothing but water and hydrochloric acid are given off. Olefiant gas is also given off in this distillation; but this perhaps proceeds only from overheating, whereby the wine-oil which runs down the sides of the retort is decomposed.

Exp. 2. From 50° to 120°, alcohol; from 130° to 135°, alcohol with ether; from 144° to 150°, alcohol with a large quantity of ether; at 152°, a very small quantity of alcohol, with large quantities of ether and water; at 160°, the same, together with small oily drops, the ether amounting to half of this distillate; at 170°, 3 pts. ether to 1 pt. water, together with a ge quantity of wine-oil; at 178°, equal parts of ether and water,

together with a large quantity of wine-oil; at 185°, 1 pt. ether to 2 pts. water, together with a large quantity of wine-oil; at 190°, water with a larger quantity of oil; from 200° to 220°, water with a pale yellow oily stratum; at 222°, the residue froths and passes over.

Exp. 3, in which the heat was raised with great care and so slowly that the experiment lasted 30 hours: At 120°, perfect ebullition; at 130°, alcohol with a small quantity of ether and a trace of hydrochloric acid; at 135°, alcohol with more ether and more hydrochloric acid; from 140° to 150°, alcohol with still larger quantities of ether and hydrochloric acid; at 155°, ether and water in equal layers, together with oily drops; from 165° to 175°, a layer of ether containing oil and a layer of water; at 186°, a layer of ether, and a layer of water 3 times as deep; from 190° to 200°, a yellowish oily liquid floating on a layer of water. In this experiment scarcely any olefiant gas was evolved.

It appears, then, that from 130° upwards, ether is produced perfectly free from chloride of ethyl; as the heat becomes stronger, the ether diminishes and the water increases, and ultimately when wine-oil begins to appear, the formation of ether ceases. Between 155° and 220°, ether passes over mixed with a large quantity of water. The first portions of wine-oil have an unpleasant odour, the latter portions a transient aromatic odour. During the whole distillation hydrochloric acid passes over, continually increasing in quantity, and the residue consists of hydrated chloride of zinc mixed with oxide. (Masson, *Ann. Chim. Phys.* 69, 240; also *J. pr. Chem.* 17, 353; abstr. *Ann. Pharm.* 31, 63.)

R. Marchand (*J. pr. Chem.* 13, 499) also, by distilling alcohol with chloride of zinc, obtained merely ether, no chloride of ethyl.

Anhydrous Chloride of Zinc distilled with *anhydrous Alcohol* yields, on the contrary, a distillate consisting almost wholly of chloride of ethyl with very little ether; in presence of water, indeed, ether is generally the chief product, but it is always accompanied by chloride of ethyl. (Kuhlmann, *Ann. Pharm.* 33, 204.)

45. *Hydrobromic* and *Hydriodic Acid* convert alcohol into bromide and iodide of ethyl (*q. v.*). — *Hydriodate of Phosphuretted Hydrogen* also forms iodide of ethyl with alcohol, giving off at the same time phosphuretted hydrogen. (Serullas.)

The anhydrous *Fixed Alkalis* decompose alcohol-vapour at a heat near to redness, forming an alkaline carbonate and a mixture of olefiant gas, marsh-gas, and hydrogen.

Such is the case with baryta when alcohol-vapour is passed over it. The olefiant gas amounts to about $\frac{4}{10}$ of the whole bulk, and may be absorbed by fuming sulphuric acid, or condensed by chlorine in the form of Dutch liquid; from the residue the marsh-gas may be separated by chlorine under the influence of light, in the form of bichloride of carbon C^2Cl^4. The first portions of alcohol probably form olefiant gas and hydrate of baryta; this substance converts the following portions of alcohol-vapour into hydrogen gas and acetate of baryta (*vid. inf.*); and this salt is decomposed by the excess of baryta, yielding marsh gas and carbonate of baryta (vid. *Acetic Acid*). (Dumas and Stas, *Compt. rend.* 20, 260; also *J. pr. Chem.* 20, 314. — *N. Ann. Chim. Phys.* 73, 158; also *Ann. Pharm.* 35, 266; also *J. pr. Chem.* 21, 378.) — According to Pelouze and Millon, (*Ann. Pharm.* 33, 183; further, *Compt. rend.* 10, 255; also *J. pr. Chem.* 19, 306), baryta at a heat near redness completely decomposes alcohol-vapour into carbonate of baryta and a gas which has the same specific

gravity as marsh-gas, consumes the same quantity of oxygen, and produces the same quantity of carbonic acid, but exhibits a different reaction with bromine. (*comp.* VII. 256.)

Alcohol vapour passed over lime at 220°, undergoes no change. (Soubeiran.)

Alcohol heated with *Hydrate of Potash* is resolved into hydrogen gas and acetate of potash:

$$C^4H^6O^2 + KO,HO = C^4H^3KO^4 + 4H.$$

To produce this decomposition, 1 pt. of hydrate of potash, which has been heated to redness, is mixed while still hot with an equal weight of powdered lime; the powder moistened with alcohol, whereby great heat is produced; the excess of alcohol driven off at 100°; and the mixture then gently heated without access of air. The mass gives off hydrogen gas mixed with a small quantity of marsh-gas, without fusion or blackening, and leaves acetate of potash. If too strong a heat were applied, the acetate of potash would also be resolved into marsh-gas and carbonate of potash. (Dumas & Stas, *Ann. Chim. Phys.* 73, 116 and 158; also *Ann. Pharm.* 35, 132; also *J. pr. Chem.* 21, 267.)

The solution of potash in alcohol absorbs oxygen from the air, forming aldehyde-resin, which colours it dark brown-red, together with acetate and formiate of potash; also carbonate of potash produced by the carbonic acid of the air.

The resin which produces the brown colour was first observed by Berthollet (*Crell. Ann.* 1786, 2, 214), and recognized as aldehyde-resin by Liebig. Chevreul (*Recherches sur les corps gras*, 322) found acetate of potash in *Potasse à l'alcool*. Hess (*Ferussac, Bull.* Sect. I, 15, 352) found no acetic acid in alcoholic potash which had become brown by exposure to the air. Arthur Connell (*N. Ed. Phil. J.* 14, 231; also *Schw.* 68, 15; abstr. *Pogg.* 31, 173) pointed out the formation of acetic and formic acid, and showed that the browning of the solution and the formation of the two acids takes place with greater rapidity, in proportion as the temperature is higher and the access of air more free; when air is blown into the hot solution, a dark red colour is formed in an hour.

The solution of potash in alcohol, as obtained in the preparation of *Potasse à l'alcool* (III, 13), if distilled to a degree of concentration which would cause it to solidify on cooling, and then further heated, froths up violently and throws up a black carbonaceous mass; the potash is then found to contain carbonate and acetate of potash. This reaction does not take place if an equal quantity of water be added before this point is attained, and the mixture then boiled down. (Liebig, *Ann. Pharm.* 23, 33.) The formation of acetic and carbonic acid may perhaps be explained as above; the black mass proceeds from the carbonization of aldehyde, which, as Liebig afterwards found, is the cause of the brown colour acquired by alcoholic potash].

It still remains to account for the peculiar taste and smell which alcohol acquires by distillation over fixed alkalis.

47. *Potassium* (or *Sodium*) immersed in absolute alcohol eliminates hydrogen gas with great evolution of heat, and forms a colourless, crystallizable compound, which may be regarded as alcohol in which 1 At. hydrogen is replaced by 1 At. metal, = $C^4H^5KO^2$, or, according to the *radical*-theory, as a compound of ether and potash = KO,C^4H^5O:

$$C^4H^6O^2 + K = C^4H^5KO^2 + H.$$

detonates less strongly, and leaves mercuric oxide. The compound blackens rapidly in direct sunshine. It dissolves in hydrochloric acid, forming a volatile substance having a pungent odour; on distilling, and adding nitrate of silver to the distillate, a soluble crystallizable substance is formed, besides chloride of silver. The original compound dissolves in sulphuric, nitric, and acetic acid, forming crystallizable substances. When boiled with a solution of sal-ammoniac, it expels ammonia and forms a crystallizable compound; a similar compound is also formed on boiling the original substance with a solution of corrosive sublimate. — When a weak alcoholic solution of potash is slowly added to an alcoholic solution of corrosive sublimate, a compound is formed different from that just described. (Sobrero & Selmi.)

When a solution of mercury in nitric acid, from which all nitrous products have been expelled by boiling, is added, at a temperature below 100°, to alcohol of 36°, in the proportion required for forming fulminating mercury, no action takes place at first; but on raising the temperature to 100°, a white crystalline compound is instantly formed, without evolution of gas. This compound contains mercuric oxide, nitric acid, carbon, and hydrogen, and when treated with hydrochloric acid, yields a volatile body having the pungent odour already mentioned. (Sobrero & Selmi, *Ann. Pharm.* 80, 108; *Compt. rend.* 33, 67; *Jahresber.* 1851, 506) — Werther and Bruckner (*J. pr. Chem.* 253, 254) did not succeed in preparing Sobrero & Selmi's yellow detonating compound. Gerhardt also (*Ann. Pharm.* 80, 111; *Jahresber.* 1851, 507) was not successful in his attempt to prepare the detonating compound; but respecting the compound formed with alcohol and nitrate of mercury, he makes the following observations:

An acid solution of *Mercurous nitrate* has no action upon alcohol; on heating the mixture nothing but a basic mercurous salt separates out. On mixing alcohol with a very concentrated solution of *Mercuric nitrate* at ordinary temperatures, there is formed a white amorphous precipitate of basic mercuric salt. If an excess of nitric acid be present, no precipitate is formed at ordinary temperatures; but on heating the liquid, the white crystalline compound observed by Sobrero & Selmi separates out, even before the boiling point is attained. This compound, when examined by the microscope, appears to consist of six-pointed stars or hexagonal tables; it is insoluble in alcohol and in water, and when heated in a small tube, decomposes with explosion but without detonation. The salt, after drying over sulphuric acid, contains $HgO,NO^5 + C^4Hg^5O,NO^5 + 2HO$, and its formation may be expressed by the equation:

$$2(3HgO,NO^5) + C^4H^6O^2 = (HgO,NO^5, + C^4Hg^5O,NO^5 + 2HO) + 4HO.$$

The liquid in which it is formed contains also a considerable quantity of mercurous nitrate, probably resulting from secondary action. — Gerhardt is of opinion that Sobrero & Selmi's detonating compound may be an alcohol in which the hydrogen is replaced by mercury. (Gerhardt, *Ann. Pharm.* 80, 111.)

49. *Chloride of Cyanogen* dissolves in alcohol in all proportions, but without exerting any immediate action upon it; but after some days, chloride of ammonium begins to separate out (in some cases the action takes place suddenly and with great violence). The decomposition is accelerated by the presence of a certain quantity of water, and by sunshine or a temperature of 80°. The liquid filtered from the chloride of ammonium contains chloride of ethyl, urethane, and carbonate of ethyl, dissolved

Table showing the amount of Absolute Alcohol in Hydrated Alcohol, by Meissner. (See his *Aräometric in ihrer Anwendung auf Chemie und Technik.* Wien 1816. Th. 2, 27.)

Alcohol.	Sp. gr. of Hydrated Alcohol, containing in 100 pts.: By Weight. At 20°.	At 17·5°.	By Volume. At 20°.	At 17·5°.
100 pts.	0·791	0·793	0·791	0·793
95 ,,	0·805	0·801	0·809	0·811
90 ,,	0·818	0·822	0·824	0·828
85 ,,	0·831	0·835	0·839	0·843
80 ,,	0·843	0·847	0·854	0·857
75 ,,	0·856	0·859	0·867	0·869
70 ,,	0·868	0·870	0·880	0·883
65 ,,	0·880	0·883	0·893	0·896
60 ,,	0·892	0·895	0·906	0·907
55 ,,	0·904	0·906	0·917	0·919
50 ,,	0·915	0·917	0·928	0·930
45 ,,	0·926	0·928	0·938	0·940
40 ,,	0·937	0·939	0·947	0·949
35 ,,	0·947	0·948	0·955	0·958
30 ,,	0·955	0·958	0·963	0·964
25 ,,	0·963	0·965	0·969	0·970
20 ,,	0·970	0·971	0·975	0·976
15 ,,	0·977	0·977	0·981	0·980
10 ,,	0·984	0·983	0·987	0·986
5 ,,	0·992	0·991	0·993	0·993
0 ,,	1·000	1·000	1·000	1·000

The following Table is given by Fownes (Manual of Chemistry, 3rd Ed., p. 591), *the specific gravities being taken at* 15·6° C, *or* 60 Fah.

Per-centage.	Sp. gr.	Per-centage.	Sp. gr.	Per-centage.	Sp. gr.
0·5	0·9991	34	0·9511	68	0·8769
1	0·9981	35	0·9490	69	0·8745
2	0·9965	36	0·9470	70	0·8721
3	0·9947	37	0·9452	71	0·8696
4	0·9930	38	0·9434	72	0·8672
5	0·9914	39	0·9416	73	0·8649
6	0·9898	40	0·9396	74	0·8625
7	0·9884	41	0·9376	75	0·8603
8	0·9869	42	0·9356	76	0·8581
9	0·9855	43	0·9335	77	0·8557
10	0·9841	44	0·9314	78	0·8533
11	0·9828	45	0·9292	79	0·8508
12	0·9815	46	0·9270	80	0·8483
13	0·9802	47	0·9249	81	0·8459
14	0·9789	48	0·9228	82	0·8434
15	0·9778	49	0·9206	83	0·8408
16	0·9766	50	0·9184	84	0·8382
17	0·9753	51	0·9160	85	0·8357
18	0·9741	52	0·9135	86	0·8331
19	0·9728	53	0·9113	87	0·8305
20	0·9716	54	0·9090	88	0·8279
21	0·9704	55	0·9069	89	0·8254
22	0·9691	56	0·9047	90	0·8228
23	0·9678	57	0·9025	91	0·8199
24	0·9665	58	0·9001	92	0·8172
25	0·9652	59	0·8979	93	0·8145
26	0·9638	60	0·8956	94	0·8118
27	0·9623	61	0·8932	95	0·8089
28	0·9609	62	0·8908	96	0·8061
29	0·9593	63	0·8886	97	0·8031
30	0·9578	64	0·8863	98	0·8001
31	0·9560	65	0·8840	99	0·7969
32	0·9544	66	0·8816	100	0·7938
33	0·9528	67	0·8793		

sparingly soluble in water, are, for the most part, quite insoluble in alcohol, so likewise are efflorescent compounds. But all deliquescent compounds; excepting carbonate of potash, phosphite of potash, and a few others, are soluble in alcohol.

Since alcohol does not dissolve all compounds which are soluble in water, it follows that many substances when dissolved in alcohol do not exhibit the same reactions towards other substances that they do when dissolved in water. Thus many acids when dissolved in absolute alcohol do not redden litmus, or decompose carbonate of lime, &c. — probably because the lime-salt which would be formed is insoluble in alcohol. In many cases, however, the action appears to be prevented by some other causes. — See the instances adduced in Vol. I., pp. 127, 128; also under the heads of *Acetic, Oxalic, Tartaric,* and *Citric acids.*

Many substances when dissolved in alcohol, impart to it the property of burning with a peculiar coloured flame: *e. g.*, boracic acid, and the salts of lithia, baryta, strontia, lime, copper, &c.

Individual Compounds.

Oxygen. — 100 vol. alcohol of sp. gr. 0·84 absorb at 18°, 16·25 vol. *oxygen gas.* (Saussure, *Gilb.* 47, 167.)

Hydrogen. — 100 vol. alcohol of sp. gr. 0·84 absorb at 18°, 5·1 vol. *hydrogen gas.* (Saussure.)

With *Water* alcohol mixes in all proportions, forming *Hydrated* or *Aqueous alcohol,* which is distinguished by various names according to its strength, *viz.*, at sp. gr. 0·83 to 0·84, *Highly Rectified Spirit, Spiritus Vini rectificatissimus,* or *Alcohol Vini;* at about sp. gr. 0·900, *Rectified Spirit, Spiritus Vini rectificatus;* and about 0·94, *Brandy, Branntwein.* — The affinity between water and alcohol exceeds many other affinities; consequently, many salts insoluble in alcohol are precipitated by alcohol from their aqueous solutions, and many compounds insoluble in water are thrown down by water from their alcoholic solutions, *e. g.*, resins, oils, &c. — Alcohol absorbs water rapidly from the air. (Yelin.) When water is placed in a basin by the side of another basin containing alcohol, and both are covered over with a bell-jar, the water absorbs the vapour of the alcohol. (Graham.) The mixture of alcohol with water is attended with evolution of heat and condensation. But hydrated alcohol of sp. gr. 0·97, when mixed with an additional quantity of water, exhibits an increase instead of a diminution of volume, still attended, however, with rise of temperature. (Thillaye, *Gilb.* 46, 194.) Absolute alcohol, on the contrary, exhibits contraction with any quantity of water whatever. This contraction is greatest when 55 vol. (1 At.) absolute alcohol are mixed with 45 vol. (6 At.) water, the mixture then occupying only 97·23 vol. instead of 100, so that the contraction amounts to 3·77 per cent. (Rudberg, *Pogg.* 13, 496; *comp.* Kapp, *Pogg.* 53, 356, who has attended more particularly to the influence of temperature.) Alcohol mixed with ice produces cold. (Tralles, *Gilb.* 38, 365.) When 1 pt. of snow at 0° is mixed with 2 pts. of alcohol at 0°, the following degrees of cold are produced, according to the percentage of absolute alcohol in the spirit: with alcohol of 99 p. c., 21°; 70 p. c., 20°; 60 p. c., 18°; 50 p. c., 16·5°; 40 p. c., 15°; 30 p. c., 12°; and 20 p. c., 8°. When equal parts of snow and alcohol are mixed, the cold produced amounts to 1° more. (R. Marchand, *J. pr. Chem.* 25, 253.)

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45 ,,	0·926	0·928	0·938	0·940
40 ,,	0·937	0·939	0·947	0·949
35 ,,	0·947	0·948	0·955	0·958
30 ,,	0·955	0·958	0·963	0·964
25 ,,	0·963	0·965	0·969	0·970
20 ,,	0·970	0·971	0·975	0·976
15 ,,	0·977	0·977	0·981	0·980
10 ,,	0·984	0·983	0·987	0·986
5 ,,	0·992	0·991	0·993	0·993
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7	0·9884	41	0·9376	75	0·8603
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15	0·9778	49	0·9206	83	0·8408
16	0·9766	50	0·9184	84	0·8382
17	0·9753	51	0·9160	85	0·8357
18	0·9741	52	0·9135	86	0·8331
19	0·9728	53	0·9113	87	0·8305
20	0·9716	54	0·9090	88	0·8279
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23	0·9678	57	0·9025	91	0·8199
24	0·9665	58	0·9001	92	0·8172
25	0·9652	59	0·8979	93	0·8145
26	0·9638	60	0·8956	94	0·8118
27	0·9623	61	0·8932	95	0·8089
28	0·9609	62	0·8908	96	0·8061
29	0·9593	63	0·8886	97	0·8031
30	0·9578	64	0·8863	98	0·8001
31	0·9560	65	0·8840	99	0·7969
32	0·9544	66	0·8816	100	0·7938
33	0·9528	67	0·8793		

Similar tables have been given by Blagden and Gilpin (*Phil. Trans.* 1794; also *Thomson's Syst. Chem.* transl. 2, 258); Lowitz (*Crell. Ann.* 1796, 1, 202); Richter (*Stöchiometrie*, 3, 280; and his *Neuere Gegenst.* 8, 77); and Tralles (*Gilb.* 38, 386); also Schrön (*Arch. Pharm.* [2], 72, 257); and F. Mayer (*Denkschr. der math. naturw. Classe der Wiener Akademie*, xx, 82; abstr. *Wien. Akad. Ber.* 1850, März, 246).

In Gay-Lussac's Alcoholometer (I, xl) the degrees indicate the number of measures of absolute alcohol contained in 100 measures of hydrated alcohol at 15°. — Körner's Alcoholometer according to per-centages by volume (*Kastn. Arch.* 22, 251; Richter's Areometer improved by Körner (*N. Tr.* 23, 11). — Strecker's Alcoholometer (*Repert.* 45, 196); Spendrup's Alcoholometer, which is divided into 16 degrees (at 11·25°) between water and highly rectified spirit. (*Schw.* 39, 475.)

For the degrees according to Beck, Cartier, and Baumé, *vid.* 1, x, xi). — According to Gilpin, 50° Bm. = 0·790 sp. gr.; 40° = 0·817; 30° = 0·867; 20° = 0·928; 10° = 1·000. — According to Sömmerring, 45° Bm. indicates absolute alcohol; 36° Bm., 80 per cent. alcohol; 31° Bm., 70 per cent.; 26° Bm., 60 per cent.; 21° Bm., 50 per cent.; 19° Bm., 40 per cent.; 16° Bm., 30 per cent.; and 14° Bm., 20 per cent.

Hydrated alcohol exposed to a great degree of cold gives up a certain quantity of its water in the solid state, this separation, however, taking place less easily as the quantity of water in the mixture is smaller. Alcohol whose strength does not exceed 33° Bm. may be frozen by the evaporation of sulphurous acid. (Bussy.)

When hydrated alcohol is exposed to warm air in a vessel tied round with a bladder; or better, inclosed in a calf's or bullock's bladder, the water alone penetrates through the bladder and evaporates, so that absolute alcohol ultimately remains; in cold moist air, alcohol enclosed in a bladder becomes more hydrated. (Sömmerring, *Denkschriften, d. k. Akad. d. Wissench. zu München*, 1811, 1814, 1820, and 1821.) — The bladder must be softened in water, washed, blown out, and entirely cleansed from fat, &c.. The ureters and urethral orifice are securely tied, and the bladder twice coated outside, and perhaps once inside, with isinglass, by which the evaporation of the alcohol is more completely prevented. The bladder is then filled with alcohol and exposed to the heat of the sun, or suspended near an ordinary stove, or over a dish of hot sand. — 4 pts. of spirit, containing 75 p. c. absolute alcohol, are then reduced to 3 pts. — If stronger spirit be used, the bladder remains dry, and only a very little alcohol evaporates; if the spirit be weaker, the bladder becomes moist, and a small quantity of alcohol escapes with the water. Absolute alcohol enclosed in a bladder evaporates very slowly; pure water very quickly, some of it oozing through in drops. The weaker the spirit, the greater is the quantity of water which evaporates in a given time. The same bladder may be used a hundred times, but it ultimately becomes stiffer, and offers greater resistance to the evaporation of the water. — This remarkable fact, discovered by Sömmerring, is due, according to that chemist, to the greater adhesion (or affinity) of the bladder for water, in consequence of which it allows the water to pass through its substance more readily than the alcohol. — These experiments of Sömmerring's have been confirmed by Van Mons (*Ann. génér. d. Scienc. phys.* 1819, 76), Geiger (*Mag. Pharm.*) 11, 141), Fr. v. Esenbeck, (*Br. Arch.* 16, 104), K. Grauer (*N. Br. Arch.* 35, 27), according to whom the evaporation takes place most quickly at a uniform temperature of about 45°); also by Meurer (*N. Br. Arch.* 35, 29); Bley, (*N. Tr.* 14, 2, 273, and *N. Br. Arch.* 35, 30.); Uterbark (*N. Br. Arch.* 35, 30); and Fr. Jahn, (*N. Br. Arch.* 35; 290.)

With this is also connected the experiment adduced by Parrots with reference to the theory of endosmose (I, 29.)

The following experiment is also distantly related to it. When

3 ounces of alcohol of sp. gr. 0·964 are placed in each of 2 cylinders of different width, so as to rise to the height of 2 inches in the wider, and 6 inches in the narrower cylinder, and the two cylinders tied over with paper, and exposed to the air till half an ounce has evaporated from each, the residue in the narrower cylinder is found to be richer in alcohol than that in the wider. (Graham, *Pogg.* 347.)

Boiling Point of Hydrated Alcohol.

According to Gröning (*Ann. Phil.* 313).						According to Yelin (*Kastn. Arch.* 2, 340). Bar. 26″ 7·19‴	
Per cent. of Alcohol.	Boiling Point.	Per cent. of Alcohol.	Boiling Point.	Per cent. of Alcohol.	Boiling Point.	Per cent. of Alcohol.	Boiling Point.
5	96·3	40	84·1	70	80·9	94	76·97
10	92·9	45	83·4	75	80·3	95	76·99
15	91·0	50	83·1	80	79·7	96	76·92
20	89·1	55	82·2	85	79·4	97	76·85
25	87·5	60	81·9	90	79·0	98	76·85
30	86·2	65	81·5	95	78·4	99	76·90
35	85·0					100	77·02

According to Yelin, therefore, alcohol of 97 to 98 per cent. boils at a somewhat lower temperature than absolute alcohol. Duflos (*Kastn. Arch.* 14, 293) regards Yelin's experiments as inconclusive, inasmuch as hot alcohol rapidly absorbs water from the air.

According to Dalton, alcohol of 43 per cent. boils at 84°.

¶. J. J. Pohl. (*Denkschriften d. math. naturw. Classe d. Wien. Akad.* II; abstr. *Wien. Akad. Ber.* 1850; März. 246; *Jahresber.* 1850, 455) has also determined the boiling point of hydrated alcohol of various strengths. He finds that, at the commencement of the ebullition, the thermometer remains constant for a short time, then slowly rises a little, and afterwards remains constant for a somewhat longer time (from 4 to 16 seconds when 14·6 grms. of liquid were used.) The temperatures at the second stationary interval are given in the following table (Bar. at 760 mm.)

Per-centage of Alcohol.	Boiling Point.	Per-centage of Alcohol.	Boiling Point.
0	100·00°	7	93·43°
1	98·79	8	92·70
2	97·82	9	92·03
3	96·85	10	91·40
4	95·90	11	90·83
5	95·02	12	90·27
6	94·21		

The presence of sugar in the liquid up to 15 p. c. appears not to exert any perceptible influence on the boiling point (a mixture of 10 pts. alcohol with 15 sugar and 75 water boiled at the same temperature as a mixture of 10 alcohol and 90 water).

Instruments, called *Ebullioscopes*, for directly ascertaining the strength of hydrated alcohol by its boiling point, have been constructed by Broissard-Vidal and by Conaty. (See a report on these instruments by Despretz, Pouillet, and Babinet, *Compt. rend.* 27, 374. A description and figure of a Vidal-instrument are given in the *Pharm. J. Trans.* 7, 166). Ure (*Pharm. J. Trans.* 7, 166; *Pharm. Centr.* 1847, 422), by means of an instrument similar to Conaty's (which is merely an ordinary thermometer, having a moveable scale which can be shifted so as to corres-

pond with the variations on the barometer, and has the percentages of alcohol marked upon it) has determined the boiling points of hydrated alcohol of different densities as follows:

Sp. gr.	B. P.	Sp. gr.	B. P.
0·9200	81·4°	0·9665	85·3°
0·9321	82·1	0·9729	87·2
0·9420	82·5	0·9786	88·8
0·9516	83.3	0·9850	91·3
0·9600	84·1	0·9920	94·4

Silbermann has proposed to determine the strength of hydrated alcohol by its rate of expansion by heat, and has constructed an instrument for the purpose. (*Compt. rend.* 27, 418; *Pharm. Centr.* 1848, 906; *Chem. Gaz.* 1849, 25). See also a description of this instrument, and of Conaty's instrument, by Bussy, *N. J. Pharm.* 15, 89.) — Another instrument for the same purpose has been constructed and described by Makin. (*Chem. Soc. Qu. J.* 2, 224.) ¶.

When weak spirit is distilled, stronger spirit passes over first, and finally nothing but water remains in the residue. According to Sömmering, a stronger spirit is obtained by distilling quickly at first than by slow distillation. A weak spirit thus distilled yields a distillate which is proportionately richer in alcohol than the product obtained by distilling a spirit already further dehydrated. Thus, when 12 per cent. spirit is distilled, the distillate contains 62 p. c. of alcohol; 28 per cent. spirit, yields 64; 40 per cent. 67; 55 per cent. 74; 70 per cent. 80; 82 per cent. 86; and 89 per cent. 90. (Sömmering.) — A mixture of 1 pt. absolute alcohol and 15 pts. water begins to boil at 93·5°; the first fiftieth which passes over is 60 per cent. spirit; the second, 54 p. c.; the third, 48 p. c.; the fourth, 42 p. c.; the fifth, 36 p. c..; the sixth, 30 p. c.; the seventh, 24 p. c.; the eighth, 18 p. c.; the ninth, 12 p. c.; and the tenth, 6 p. c. spirit; — so that of the first ten-fiftieths of the distillate, each one contains 6 p. c. less alcohol than the preceding.

Alcohol, notwithstanding its lower boiling point, cannot be entirely freed from water by repeated distillation; the strongest spirit thus obtained has, according to Saussure, a density of 0·8248; according to Sömmering, a percentage of 90; according to Joss (*Schw.* 69, 337), a density of 0·820 (or about 90 p. c.); according to Soubeiran, a per-centage of 92·6. For since, according to I, 266, an elastic fluid, at any given temperature, promotes the evaporation of another body below the boiling point of the latter, the alcohol vapour produced by heating hydrated alcohol takes up a quantity of aqueous vapour corresponding to its volume and temperature, below the boiling point of the water, and the two pass over together and are condensed.

Nearly absolute alcohol, subjected to fractional distillation, gives off first hydrated, and then absolute alcohol. (Sömmerring). Confirmed by Yelin, Fuchs, and Duflos. (*Kastn. Arch.* 14, 291). If, from 100 pts. of 98·5 per cent. alcohol, successive portions of 10 to 13 parts be distilled off till only 20 pts. remain, the first distillate has, at 21°, a density of 0·7965; the second, 0·7945; the third and fourth, 0·7950; the fifth, 0·7935; the sixth, 0·7915; the seventh, 0·7910; and the residue, 0·7905. (Duflos.) — This result is also probably due to the evaporation of water in an atmosphere of alcohol vapour. The adhesion of the first-formed portions of alcohol vapour to the aqueous vapour induces the formation of the latter as long as any water remains, and thus the remaining alcohol *becomes* continually stronger. Yelin explains this phenomenon by the

—Alcohol dissolves *Sulphide of Carbon*, and the solution is not decomposed by water. — Liquid *Sulphide of Phosphorus*, shaken up with 80 p. c. alcohol, forms a colourless liquid, which is not altered by exposure to sunshine. Water makes it milky by separating particles of phosphorus, which, on exposure to sunshine, turn first yellow and afterwards reddish yellow, whilst an alliaceous odour of phosphorous acid and sulphuretted hydrogen is evolved, the presence of the latter being also recognizable by its action on the heavy metals. (R. Böttger, *J. pr. Chem.* 12, 365.)

Selenium.—Selenious acid is dissolved readily and abundantly by alcohol. (Berzelius.)

Iodine. — Alcohol dissolves *Iodine* quickly and in large quantity, forming a dark brown volatile solution, from which water throws down the iodine in small crystals, which at first have a reddish tint. (Vauquelin, *Ann. Chim.* 90, 249.) The solution gradually decomposes, yielding hydriodic acid and iodide of ethyl. (Colin, Le Royer.) The iodine may be dissolved out by agitation with mercury, but, unless the solution be mixed with a double quantity of water, a small quantity of iodide of mercury remains in solution, even when the mercury is in excess. But if the mixture be shaken up for two minutes with copper filings, all the free iodine is removed, the liquid becoming colourless and retaining only the hydriodic acid and iodide of ethyl which have been formed by standing. (Herzog, *N. Br. Arch.* 40, 37.) Absolute alcohol saturated with sulphurous acid gas dissolves a much larger quantity of iodine than pure alcohol; on exposing the brown solution to the sun, sulphur crystallizes out in prisms half an inch long, an effect which is not produced unless iodine be present. (Döbereiner, *Repert.* 15, 419.) — *Iodic acid* dissolves very sparingly in alcohol, and is therefore precipitated by alcohol from its aqueous solution. (Serullas, *Ann. Chim. Phys.* 45, 70.)— *Periodic acid* dissolves very readily. Alcohol mixes with aqueous *Hydriodic acid*, and doubtless absorbs hydriodic acid gas in large quantity.

Chlorine. — 100 pts. alcohol of 36° Bm. absorb at 12·5°, 68 pts. of *Hydrochloric acid gas*, the temperature rising to 17·5°. The product is a colourless, oily, fuming, very acid liquid of sp. gr. 1·134, which boils and gives off chloride of ethyl at 37°, mixes, without rise of temperature, with a mixture of alcohol and oil of vitriol, but when mixed with water, becomes hot and gives off bubbles of chloride of ethyl having an ethereal odour. (Boullay, *Ann. Chim.* 63, 90; also *N. Gehl.* 4, 37.) During the absorption of the hydrochloric acid gas, and also on gently heating the compound, a gas is evolved which burns with a green flame and produces vapour of hydrochloric acid. (Gehlen, *A. Gehl.* 2, 224.) [Probably a mixture of hydrochloric ether vapour and common air]. — 100 vol. alcohol absorb 1·200 vol. *Phosgene gas.* — Alcohol absorbs gaseous *Chloride of Boron.* — With Berzelius & Marcet's *camphoroïdal compound* (II, 337, and VII, 358), it forms a liquid which reddens litmus, has an unpleasant and very sour taste; dissolves zinc with evolution of a stinking gas; gives off, when distilled, sulphurous acid, carbonic acid, alcohol, and chloride of ethyl; is for the most part precipitable by water; and does not precipitate an alcoholic solution of nitrate of silver till after some time. (Berzelius.)

Fluorine. — 1 pt. of absolute alcohol impregnated at 0° wit the

Hydrofluoric acid evolved from 1 pt. of fluor spar and 2 pts. oil of vitriol acquires a yellowish colour, smells and tastes sour and like horse-radish. Water added to the mixture does not form any precipitate, but by partial distillation, the liquid yields a distillate which appears to contain fluoride of ethyl together with alcohol. (Reinsch. *J. pr. Chem.* 19, 314). — Alcohol liquid Bm. saturated with gaseous *Fluoride of Boron*, forms a very acid of 42° which fumes strongly in the air. (Desfosses.) — Absolute alcohol absorbs the gas abundantly and with rise of temperature, and finally solidifies in the form of a clear fuming jelly. On addition of caustic potash, the mixture does not yield any layer of ether, but acquires an agreeable odour different from that of ether, and when distilled, gives off nothing but alcohol. (Liebig, *Pogg.* 24, 171.) For Kuhlmann's statements, *vid.* pp. 245, 246

Nitrogen. — 100 vol. alcohol of sp. gr. 0·84 absorb at 18°, 4·2 vol. *Nitrogen gas.* (Saussure.) — Absolute alcohol exposed to the air takes up 0·11 of its volume of gas, $\frac{1}{3}$ of which is oxygen and $\frac{2}{3}$ nitrogen, and $\frac{2}{3}$ of which is expelled on addition of an equal quantity of water. (Döbereiner, *Gilb.* 72, 432.) — 100 vol. alcohol of sp. gr. 0·84, absorb at 18°, 15·3 vol. *Nitrous oxide gas.* (Saussure.) — Alcohol absorbs nearly its own volume of *Nitric oxide gas*, which cannot be again expelled by heat. (Priestley.) — 3 pts. alcohol of 38° Bm. absorb about 1 pt. of ammoniacal gas. (Boullay.) — 1 vol. alcohol of sp. gr. 0·829 absorbs about 50 vol. ammoniacal gas. (J. Davy, *N. Ed. Phil. J.* 16, 254.) The gas is driven out again by gentle heat. — Alcohol dissolves *Iodide of ammonia* (*Iod-ammoniak*). — It dissolves *Monocarbonate of ammonia* (J. Davy), *Hypophosphite of ammonia*, and *Hydrosulphate of ammonia*. — *Sulphate of ammonia* does not dissolve in absolute alcohol; but at 14°, it dissolves in 500 pts. alcohol of sp. gr. 0·872, and in 62·5 pts. of alcohol of sp. gr. 0·905. (Anthon.) — *Hydriodate of ammonia* dissolves abundantly; *Hydrobromate* and *Hydrochlorate of ammonia* also dissolve, the latter in 14 pts. of highly rectified spirit at a boiling heat. (Wenzel.) *Chlorate of ammonia* dissolves readily, the *Perchlorate* sparingly. The compounds of *Ammonia* with *Phosgene, Dichloride of Sulphur*, and *Fluoride of Boron*, also dissolve in absolute alcohol; so likewise do the *Hydrofluate* and *Nitrate of Ammonia* (the latter in 1·1 pt. at a boiling heat according to Wenzel).

METALS. — Alcohol dissolves only those metallic oxides which possess either an alkaline or an acid character. Of the metallic sulphides it dissolves only those of potassium and sodium; of the iodides and bromides it dissolves a somewhat greater, and of the chlorides a still greater number. The carbonates, borates, phosphites, phosphates, hyposulphites, sulphites, hyposulphates, sulphates, iodates, and periodates, it dissolves either not at all or in very small quantity. The only sulphates which dissolve readily in alcohol are those of ferric and platinic oxide. On the other hand, alcohol dissolves many hypophosphites, a still greater number of bromates, chlorates, and perchlorates, and very many nitrates.

Potassium. — When Gay-Lussac's pyrophorus (prepared with charcoal and sulphate of potash), which contains charcoal, *sulphide of potassium*, and dry *potash*, is boiled with absolute alcohol, the filrate first yields crystals of alcoholic potash, then colourless prisms of sulphide of potassium containing alcohol. Both compounds are converted into acetate of potash by exposure to the air. The crystals of the former when heated first give off alcohol, then above 250°, turn somewhat brown, and give off hydrocarbons in large quantity. (Kuhlmann, *Ann. Pharm.*

33, 103.) [Are these crystals potash + alcohol, or are they $C^4H^5KO^2$? *comp.* p. 255] — *Hydrate of potash* dissolves abundantly in strong alcohol, forming *Alcoholic potash*, an oily, heavy, very caustic liquid, which is colourless at first but soon turns yellow and reddish brown (p. 254). — When strong potash-ley is distilled with alcohol till even the water has passed over, the residue, on being neutralized with sulphuric acid and distilled, gives up an additional quantity of alcohol, which must, therefore, have been kept back by the potash. (Boullay.) — The solution of hydrate of potash in alcohol of 25 to 30 p. c. is separated by agitation with ether into two layers, the lower consisting of aqueous potash, and the upper of ether containing alcohol. If the alcohol be strong, the ether separates only a small quantity of potash, the greater part remaining dissolved in the mixture of alcohol and ether; it may, however, be completely separated by agitation with water. (Döbereiner, *Ann. Pharm.* 14, 248.) — Alcohol dissolves *Sulphide*, *Sulphocarbonate* (very sparingly), *Iodide*, *Bromide* (sparingly), *Chloride* (in 48 parts at a boiling heat, according to Wenzel), and *Fluoride of Potassium*. Chloride of potassium is precipitated in delicate crystals from its alcoholic solution by ether. (Döbereiner.) — *Monocarbonate of Potash* dissolves only in very dilute alcohol, and abstracts the water from stronger spirits, forming a layer below the alcohol. 1 pt. of carbonate of potash dissolves in 9 pts. of alcohol of 17° Bm.; a larger quantity of carbonate of potash added to this solution dehydrates the alcohol, and consequently precipitates the portion of the salt previously dissolved, and forms a watery layer below the alcohol. Concentrated carbonate of potash (*Oleum Tartari*) shaken up with alcohol of 20° Bm. takes up small quantities of water and alcohol, and becomes turbid whenever it is heated, the alcohol being each time separated out. (Guibourt, *J. Pharm.* 13, 103.) — Alcohol dissolves *bicarbonate of potash* (very sparingly and only at a boiling heat), hypophosphite (abundantly), *bromate* and *chlorate* (both very sparingly), and *nitrate* (in 48 pts. at a boiling heat,—Wenzel). Neutral sulphate of potash is insoluble even in alcohol of sp. gr. 0·905. (Anthon.)

Sodium. — *Hydrate of soda* forms with alcohol a solution similar to alcoholic potash. Alcohol dissolves *Sulphide of sodium* sparingly, the *sulphocarbonate* abundantly, and the *iodide*, *bromide*, *chloride*, *fluoride*, and *fluoboride* very sparingly. It dissolves *hypophosphite of soda* very abundantly, the *phosphite* and *chlorate* sparingly, and the *nitrate* (in 10 pts. at a boiling heat,—Wenzel.) Chloride of sodium is precipitated from its alcoholic solution by ether in delicate crystals.

Lithium. — *Hydrate of lithia* dissolves very sparingly in alcohol, and is partially precipitated by alcohol from its aqueous solution. (C. G. Gmelin.) Alcohol dissolves *sulphide of lithium*, and very abundantly the *chloride of lithium* and *nitrate of lithia*.

Barium. — *Anhydrous baryta* placed in contact with absolute alcohol forms fern-like laminæ in the course of 24 hours. These crystals turn yellow after a while; when heated, they first give off alcohol, then blacken slightly and evolve bicarburetted hydrogen [olefiant gas!], together with a small quantity of quadrocarburetted hydrogen [benzol!], a yellowish empyreumatic oil, and water (never ether), and finally leave white carbonate of baryta. (Kuhlmann, *Ann. Pharm.* 33, 104.) — 1 pt. hydrate of baryta dissolves in 150 to 200 pts. of boiling alcohol. (*Berzelius, Lehrb.*) Baryta-water is not clouded by alcohol. — Alcohol, if

nearly absolute, readily dissolves *iodide* and *bromide of barium*; cold alcohol dissolves $\frac{1}{8000}$ and hot alcohol $\frac{1}{5000}$ pt. of *chloride of barium*, and *perchlorate of baryta* in considerable quantity.

Strontium. — Alcohol dissolves *strontia* in very small quantity only, the *chloride of strontium* in moderate quantity, and the *chlorate* and *perchlorate of strontia* abundantly.

Calcium. — Boiling alcohol dissolves a trace of *lime* sufficient to turn reddened litmus blue, and form a cloud with oxalic acid. (Bonastre, *J. Pharm.* 10, 9.) When the alcohol is distilled off from the lime, a large quantity of it remains combined, not escaping even at 130°. (Liebig.) Alcohol produces considerable turbidity in lime-water. It dissolves a trace of *carbonate of lime*, sufficient to turn reddened litmus blue. (Grischow, *Schw.* 27, 26.) It dissolves *bromide of calcium*, and very abundantly *chloride of calcium*, and *chlorate, perchlorate*, and *nitrate of lime*. Chloride of calcium deliquesces in vapour of absolute alcohol. It dissolves in absolute alcohol very abundantly and with great evolution of heat, which is often sufficient to make the alcohol boil. At 78·3°, 1 pt. chloride of calcium dissolves in 1·43 pts. absolute alcohol. A solution of 1 pt. dry chloride of calcium in 5 pts. absolute alcohol, boiled down to a state of great concentration, gradually yields on cooling, small, transparent, colourless, very soft needles, or often delicately striated tables, mostly three-cornered. They contain 41 p. c. chloride of calcium to 59 p. c. alcohol [therefore 1 At. chloride of calcium to 2 At. alcohol]. They give up their alcohol completely at 121°. They deliquesce in the air. The solution which boils at 90·55°, has also a similar composition. A solution of 4 pts. chloride of calcium in 10 pts. absolute alcohol yields no crystals even at 45·6°, but crystallizes completely in the cold. The presence of water disturbs the crystallization, so that it takes place with difficulty when the alcohol contains even 1 per cent. of water only, and not at all with alcohol of sp. gr. 0·827. If water be present, the compound does not give up its alcohol till it is heated considerably above 121°, the residue, in fact, still containing traces of alcohol, even after being heated for several hours to a tempetature between 205° and 260°. (Graham.) The solution of chloride of calcium in an equal quantity of alcohol, which by itself would boil at 82·5°, boils at 85°. (Duflos.) Absolute ether added in excess precipitates chloride of calcium from its solution in absolute alcohol; when less ether is added, a small quantity of chloride of calcium remains in solution, but separates out again, producing a strong turbidity every time the liquid is heated, if only by the hand, and redissolves on cooling. Similarly with nitrate of lime. (Döbereiner, *Ann. Pharm.* 14, 249.) 1 vol. absolute alcohol saturated with chloride of calcium, forms a clear mixture with 6 vol. ether; but if 12 vol. ether be added, the mixture becomes turbid, and deposits chloride of calcium, probably as an alcoholate, in the form of a white powder. When 1 vol. of an aqueous solution of chloride of calcium saturated in the cold is mixed with 1 vol. absolute alcohol, the mixture shaken up with 1 vol. absolute ether, and then left at rest, two layers of equal depth are formed, the lower consisting of aqueous chloride of calcium containing alcohol, and the latter of a mixture of alcohol and ether. If 1 vol. more ether be added, the mixture briskly shaken, and then left at rest, there are formed 1 vol. of a lower stratum consisting of aqueous chloride of calcium, and 3 vol. of an upper stratum consisting of alcohol containing

ether. On the other hand, 1 vol. aqueous chloride of calcium, 2 vol. alcohol, and 1 vol. ether, form a uniform mixture. Hence the chloride of calcium takes up the water by preference, the ether taking up the alcohol; and when no water is present, the ether takes the alcohol from the chloride of calcium. (Döbereiner.) ¶ A saturated solution of chloride of calcium in hot alcohol of sp. gr. 0·795 at 20° (containing about 1 p. c. of water) does not deposit crystals on cooling: the liquid evaporated to a syrupy consistence, yields on cooling a white solid mass, which, after being pressed between bibulous paper, is soft and deliquescent, and contains 60·6 p. c. chloride of calcium. A solution of chloride of calcium in alcohol of sp. gr. 0·795 at 20°, left for some days over sulphuric acid in vacuo, became thick and viscid, without depositing crystals; when part of it was cooled in ice, a crystalline tallowy mass was obtained, which, when freed as much as possible from adhering liquid by pressure, contained $2CaCl+2C^4H^6O^2+2HO$ (with 60·4 p. c. chloride of calcium); the remainder being left in vacuo, became dry and solid after 12 days, and then contained 60·5 p. c. chloride of calcium. By dissolving chloride of calcium in warm alcohol of sp. gr. 0·790 at 23°, rapidly filtering the solution, and cooling the filtrate in ice, a soft, white, crystalline substance was obtained, which, after being well pressed, had the composition $CaCl+2C^4H^6O^2$. (Chodnew, *Ann. Pharm.* 71, 241; *Jahresber.* 1849, 409). ¶ A saturated solution in absolute alcohol of *nitrate of lime*, previously dried over a spirit-lamp, becomes viscid on cooling, and after being left for some days, solidifies during a cold night in the form of a slightly moist, crystalline mass, which, after being dried and pressed, contains 58·97 p. c. nitrate of lime and 41·03 alcohol, therefore somewhat more than 1 At. alcohol to 1 At. lime-salt. (Graham.) 2 vol. ether added to 1 vol. of a saturated solution of nitrate of lime in absolute alcohol form no precipitate; but 15 vol. ether precipitate the lime-salt, partly in the crystalline form, partly as a liquid alcoholate. (Döbereiner.)

Magnesium. — Boiling alcohol dissolves a trace of *magnesia* sufficient to turn reddened litmus blue. (Bonastre.) None of the other earths are soluble in alcohol. Alcohol dissolves *chloride of magnesium*, *chlorate of magnesia*, and *nitrate of magnesia* in considerable quantities. Chloride of magnesium forms an alcoholate with alcohol. Nitrate of magnesia dried till it begins to decompose, dissolves in 4 pts. of absolute alcohol at 15·6°, and in 2 pts. of boiling alcohol. A solution saturated while hot, deposits, on cooling, a crystalline mass of sp. gr. between 1·00 and 1·10, which is much harder than the chloride of calcium compound, and contains 74 pts. (1 At.) nitrate of magnesia to 205 pts. ($4\frac{1}{2}$ At.) alcohol. The compound melts when suddenly heated, and gives off, first alcohol, then nitrous fumes; when carefully heated, it dries up without loss of acid. (Graham.) ¶ Chodnew, by dissolving anhydrous nitrate of magnesia in alcohol of 0·795 at 20°, boiling the solution, filtering in the boiling hot state, and leaving the filtrate to cool, obtained a white mass, like margarin, which fused when heated, and after being freed from liquid as much as possible by pressure, was found to contain $MgO,NO^5+3C^4H^6O^2$. A solution of anhydrous nitrate of magnesia in alcohol left to evaporate in the air, always absorbs moisture, and ultimately yields crystals of nitrate of magnesia with 6 At. water. (Chodnew.) ¶

Cerium. — The only cerous salts that are soluble in alcohol are the *chloride* and the *nitrate*. Nothing is known about the solubility of inorganic *Lanthanum-compounds* in alcohol.

Iodide of yttrium dissolves sparingly in alcohol. — *Chloride of glucinum* and *nitrate of glucina* readily. — *Bromide of aluminum, chloride of aluminum* and *nitrate of alumina* abundantly; *chlorate of alumina* moderately. — *Chloride of thorinum* also dissolves in alcohol, and *chloride of zirconium* abundantly.

Silicium. — Absolute alcohol absorbs gaseous *fluoride of silicium* in considerable quantity, becoming heated thereby, and remaining liquid (this fact is confirmed by Liebig & Wöhler, *Pogg.* 24, 172); it acquires the odour of the gas, and its density is increased to 1·02; if the alcohol contains water, it becomes gelatinous on cooling, and gives off an ethereal odour. (Unverdorben, *N. Tr.* 9, 1, 32.) Alcohol absorbs more than its own weight of gaseous fluoride of silicium, and solidifies, when near saturation, to a transparent jelly having an ethereal odour. (Berzelius, *Pogg.* 1. 180.) The compound, when prepared with absolute alcohol, begins to boil at 80°, and passes over unchanged between 150° and 160°, the boiling point gradually rising. It burns away with a red flame, giving off a white smoke, and depositing silica. It is decomposed by water, and more readily by aqueous potash, the odour evolved in the decomposition being merely that of alcohol. (Kuhlmann, *Ann. Pharm.* 33, 207.)

There are no known compounds of *Titinium, Tantalum,* or *Tungsten,* which are soluble in alcohol.

Molybdenum. — The *brown* and *green oxides of molybdenum* dissolve sparingly in alcohol; *molybdate of terchloride of molybdenum* more freely.

Vanadium. — *Green oxide of vanadium* and *vanadic acid* dissolve very sparingly in alcohol of sp. gr. 0·80, and are quite insoluble in absolute alcohol. *Vanadic sulphate* is insoluble in absolute alcohol, but dissolves abundantly in alcohol of sp. gr. 0·833. *Terchloride of vanadium* dissolves more abundantly, and, after dissolving, decomposes. *Bifluoride of vanadium* dissolves in absolute alcohol, forming a greenish solution.

Chromium. — Crystallized *chromic acid* dissolves in cold alcohol [probably when a large quantity of alcohol is poured upon it all at once (*comp.* p. 243)], decomposition not taking place till the mixture is heated. (Unverdorben, *N. Tr.* 9, 1, 31.) *Sesquichloride of chromium* is also soluble in alcohol.

Uranium. — Alcohol dissolves the *sulphate, hydrochlorate,* and *nitrate of uranic oxide.*

Manganese. — *Chloride of manganese,* and the *perchlorate* and *nitrate of manganous oxide* dissolve readily. The chloride dissolves abundantly in absolute alcohol, and after saturation at a high temperature, yields an alcohol-compound in tables with truncated edges, and containing 64 pts. (1 At.) chloride of manganese to 58 pts. ($1\frac{1}{4}$ At.) alcohol. (Graham.) 1 pt. of dry chloride of manganese dissolves between 11° and 37° in 2 pts. and at 76° in 1·7 pt. of absolute alcohol; 1 pt. of crystallized chloride of manganese, containing 4 At. water, dissolves at 10° in 1·75; at 25° in 0·75; at 44° in 0·69; and 84° in 0·97 pts. of 75 per cent. alcohol. The white needles which separate from a hot solution of chloride of manganese

in absolute alcohol contain 43·33 p. c. (1 At.) alcohol to 56·67 p. c. (1 At.) chloride of manganese. The alcoholic solution of chloride of manganese is green when prepared hot. (Brandes, *Pogg.* 22, 266.) The solution burns with a red, sparkling flame. (John.) From 1 measure of absolute alcohol saturated with chloride of manganese, the chloride of manganese is completely precipitate in the form of powder by the addition of 15 to 20 measures of ether. (Döbereiner.)

Arsenic.—*Arsenious acid* dissolves very sparingly in absolute alcohol at ordinary temperatures. (A. Vögel, *J. pr. Chem.* 4, 236). When 1 pt. of the pulverized acid is immersed for thirty days in 10 to 40 pts. of (absolute?) alcohol, a solution is gradually formed containing 1 pt. of the acid in 60 pts. of alcohol. When 1 pt. of the acid is immersed in 60 or 150 pts. of alcohol, a solution is formed containing 1 pt. of acid in 124 or 140 pts. of alcohol. (N. Fischer, *Kastn. Arch.* 11, 235.) 1 pt. of arsenious acid dissolves in 80 pts. of boiling highly rectified alcohol. (Wenzel.) — *Arsenic acid* dissolves more abundantly. — *Chloride* and *fluoride of arsenic* are miscible with alcohol.

Antimony.—*Terchloride of antimony* dissolves in absolute alcohol.

Tellurium.—Crystallized *telluric acid* is insoluble in absolute alcohol, but slightly soluble in hydrated alcohol, the quantity dissolved increasing with the proportion of water. The solution is not decomposed by boiling. (Berzelius.) — *Biniodide of tellurium* dissolves in alcohol, but with partial decomposition, even when the alcohol is absolute. (Berzelius.)

Zinc.—Alcohol dissolves *bromide, chloride, chlorate,* and *nitrate of zinc.* — The chloride dissolves abundantly in hot absolute alcohol; the yellowish solution, when sufficiently evaporated, becomes viscid like turpentine on cooling, and deposits small, soft, yellowish crystals, containing 11·9 pts. ($\frac{1}{2}$ At.) alcohol to 67·4 pts. (1 At.) chloride of zinc; when heated, they fuse partially and give off the alcohol. The mother-liquid above the crystals contains 7 pts. of alcohol to 20 pts. chloride of zinc. (Graham.) — Chloride of zinc not completely dehydrated dissolves abundantly in alcohol of 36° Bm., with great evolution of heat, and forms a transparent, dark brown liquid. (Masson.)

Cadmium.—Alcohol readily dissolves *iodide, bromide, chloride, perchlorate,* and *nitrate of cadmium.*

Tin. — The solution of *stannic iodide* in absolute alcohol, yields, on the addition of water, a precipitate of hydrated stannic iodide. (Döbereiner, *Schw.* 26, 381 to 382.) — *Protochloride of tin* dissolves readily in absolute alcohol, especially when hot. The clear solution becomes syrupy on cooling, smells after a while of acetic ether, and remains unaltered in the air for a considerable time. (Capitaine, *J. Pharm.* 25, 552.) — The alcoholic solution of *bichloride of tin* deposits the hydrated bichloride on the addition of water. (Döbereiner.) The mixing of bichloride of tin with absolute alcohol is attended with great rise of temperature, and the mixture, as it cools, deposits colourless, silky needles, which, when freed from excess of alcohol by being kept over lime in a receiver containing air, fuse at 75°, have an aromatic odour, and do not fume in the air at ordinary temperatures. Water instantly separates the alcohol from the compound. — A mixture of 2 At. bichloride of tin with 1 At. alcohol yields numerous crystals and a mother-liquid consisting of excess of the

bichloride.—A solution of 100 pts. (1 At.) of bichloride of tin in 32·84 pts. (about 0·9 At.) alcohol, changes on cooling, to a solid, crystalline mass, which melts between 70° and 75°.—A solution of 1 At. bichloride of tin in 1 At. absolute alcohol solidifies on cooling to a doughy mass; with $1\frac{1}{4}$ At. alcohol, the mixture becomes semifluid; and with 2 At. alcohol, crystals are obtained together with a mother-liquid consisting of alcohol. (Kuhlmann, *Ann. Pharm.* 33, 106, and 192.)—The small prisms readily soluble in alcohol, which are obtained from the mixture at temperatures below 0°, contain, after being dried for a short time in vacuo over oil of vitriol and hydrate of potash (if left too long in the vacuum they decompose), 14·25 p. c. C, 3·76 H, 12·32 O, 36·78 Sn, and 32·89 chlorine; they are therefore $=C^8H^{12}O^5Sn^2Cl^3=2C^4H^6O^2,Sn^2Cl^3O$, *i. e.* a compound of alcohol with a bichloride of tin, in which $\frac{1}{4}$ of the chlorine is replaced by oxygen. (Lewy, *Compt. rend.* 21, 371; abstr. *J. pr. Chem.* 37, 481.) [If the analysis be correct, it is probable that hydrochloric ether and water are formed at the same time:

$$3C^4H^6O^2 + 2SnCl^2 = C^8H^{12}O^5Sn^2Cl^3 + C^4H^5Cl + HO.]$$

None of the inorganic compounds of *Lead* appear to be soluble to any considerable extent in alcohol.

Iron.—Alcohol dissolves *protochloride* and *sesquichloride of iron* (probably also the iodide and bromide), and the *tersulphate* and *ternitrate of ferric oxide.*—Protochloride of iron forms a crystalline compound with absolute alcohol; so, likewise, does the sesquichloride; the latter retains the alcohol with great tenacity. (Graham.) Protochloride of iron dissolves but sparingly in a mixture of alcohol and ether. (Kerner.)—Sesquichloride of iron dissolves in absolute alcohol with great rise of temperature, and yields crystals on cooling, though with considerable difficulty. The solution in equal numbers of atoms solidifies on cooling, into a viscid mass, which becomes more fluid when heated. (Kuhlmann, *Ann. Pharm.* 33, 106, and 200.)—The saturated solution of sesquichloride of iron in absolute alcohol is not precipitated by 15 or 20 times its volume of ether; water subsequently added, throws up, though with difficulty, a layer of aqueous sesquichloride of iron. (Döbereiner.)

Cobalt.—The solution of *iodide of cobalt* in absolute alcohol is dark green; in hydrated alcohol, light red.—The blue solution of *chloride of cobalt* in absolute alcohol, likewise turns red on addition of water. 1 vol. of absolute alcohol saturated with chloride of cobalt forms, with 15 or 20 vol. ether, a clear, light blue mixture, which, when shaken up with water, separates into two layers, the upper of which is ethereal and colourless, while the lower, which contains aqueous chloride of cobalt, is red. Ether added in excess to alcohol, saturated at the same time with chloride of cobalt and chloride of manganese, throws down only the latter, so that by this method, with due precaution, a separation of cobalt from manganese may be effected. (Döbereiner.)—*Nitrate of cobalt* dissolves in its own weight of cold highly rectified alcohol. (Wenzel.)

Nickel.—*Iodide of nickel* dissolves slowly in absolute alcohol, more readily in hydrated alcohol, forming a light green solution. (Erdmann.)—Alcohol dissolves *bromide* and *chloride of nickel.* *Nitrate of nickel* is insoluble in absolute alcohol (p. 219), but dissolves in hydrated alcohol.

Copper.—Alcohol dissolves considerable quantities of *cupric chloride*,

perchlorate, and *nitrate*, and moderate quantities of *cuprico-ammonic* and *cuprico-potassic chloride*.

Mercury. — *Protoiodide of mercury* dissolves in 36 parts of alcohol (Saladin, *J. Chim. méd.* 7, 530); the colourless solution in alcohol of 36° Bm. is precipitated by water. (N. E. Henry, *J. Pharm.* 8, 105). — *Protobromide of mercury* dissolves very abundantly. (Balard.) — *Protochloride of mercury* dissolves in 2½ pts. of cold alcohol (Richter); in 3 pts. (Karls); in 2 pts. alcohol of sp. gr. 0·816 at 15·6°, forming a solution of sp. gr. 1·08; and the warm saturated solution deposits needles on cooling. (J. Davy, *Phil. Trans.* 1822, 359.) 1 pt. of corrosive sublimate dissolves at 10° in 2·57 pts. alcohol of 39° Cartier, in 2·9 pts. of 38°, in 3·6 pts. of 35°, in 4·2 pts. of 30°, in 9·3 pts. of 22°, and in 14·6 pts. alcohol of 15° Cartier. (N. E. Henry, *Bull. Pharm.* 3, 194.) On mixing a saturated solution of corrosive sublimate in absolute alcohol with one-fourth of its bulk of water, the greater part of the corrosive sublimate is precipitated. (Döbereiner.)

Silver. — Alcohol dissolves small quantities of *chlorate*, larger quantities of *perchlorate* and *nitrate of silver*.

Gold. — Alcohol dissolves *terchloride of gold* and reduces it gradually, more quickly under the influence of light and heat. It readily dissolves *bromo-aurate* and *chloro-aurate* of *potassium*.

Platinum. — Alcohol readily dissolves *platinic sulphate, iodide*, and *chloride*, also the *iodoplatinate, bromoplatinate*, and *chloroplatinate of sodium*, — and very small quantities of the *chloroplatinates of ammonium* and *potassium*. — Between 15° and 20°, one part of chloroplatinate of ammonium dissolves in 26,535 parts of 97·5 per cent. alcohol, in 1,406 pts. of 76 per cent. alcohol, and in 665 pts. of 55 per cent. alcohol; if, however, free hydrochloric acid be present, it dissolves in 672 parts of 76 per cent. alcohol. 1 pt. of chloroplatinate of potassium dissolves in 12,083 pts. of 97·5 per cent. alcohol, in 3,775 pts. of 76 per cent. alcohol, and in 1,0[illegible] pts. 55 per cent. alcohol; and if a small quantity of free hydrochloric acid be present, in 1,835 pts. of 76 per cent. alcohol. (Fresenius, *Ann. Pharm.* 59, 117.)

Palladium. — Alcohol dissolves *protochloride of palladium*, and the *chloropalladiates of potassium, sodium, barium, calcium, magnesium*, and *manganese*.

Rhodium. — Alcohol dissolves *sesquichloride of rhodium* and *chlorrhodiate of ammonium*.

Iridium. — Alcohol readily dissolves *bichloride of iridium*, also *chloriridite* and *chloro-iridiate of sodium;* in the hydrated state, it also dissolves *chloro-iridite of ammonium*.

Osmium. — From the colourless solution of *osmic acid* in alcohol, the osmium is gradually reduced. Moreover, alcohol dissolves *sesquichloride of osmium and ammonium*, and *protochloride of osmium and potassium*.

Alcohol absorbs considerable quantities of the *gaseous oxide, bromide* and *chloride of Methyl*. It mixes in all proportions with *wood-spirit*

yet to be considered, the following general observations may be made:

Alcohol dissolves all Hydrocarbons, and therefore the Primary Nuclei and any compounds which those nuclei may form with hydrogen.— Among the compounds which likewise contain oxygen, alcohol dissolves especially those in which the number of atoms of all the elements together is comparatively small, and the oxygen is in comparatively small proportion; — hence it is more inclined to dissolve aldides (in which class may be included many volatile oils, camphors, and resins) and acids of small atomic weight, than acids of greater atomic weight or richer in oxygen. Acids which are but slightly soluble or quite insoluble in alcohol, likewise yield salts of similar character. Acids containing but little oxygen, and their salts, often dissolve in alcohol more readily than in water. — Compounds in which hydrogen is replaced by iodine, bromine, or chlorine, do not appear to have their solubility in alcohol diminished by the substitution; even the chlorides of carbon are all soluble in alcohol. — All compounds of carbon, hydrogen, and nitrogen, *e. g.*, the non-oxygenated alkaloids, are soluble in alcohol; but with regard to compounds of this nature containing oxygen, the observations above made concerning the influence of oxygen likewise hold good.

Aldehyde. C^4H^4,O^2.

LIEBIG. *Ann. Pharm.* 14, 133; also 36, 376.

This compound is called Aldehyde, because it may be regarded as alcohol deprived of part of its hydrogen, *Al*cohol *deh*ydrogenatum. [*Nevine.*]

Döbereiner (pp. 207, 244) found that when alcohol is slowly burned in contact with platinum, or oxidated by a mixture of sulphuric acid with peroxide of manganese or chromic acid, peculiar products are formed, which he designated by the terms *Light* and *Heavy Oxygen Ether;* but as he did not succeed in obtaining these compounds in a state of purity, the manner in which he characterized them was indefinite and somewhat confused. (*Schw.* 32, 269; 32, 124; 38, 327; 64, 466.) It afterwards appeared that the term *heavy oxygen-ether* really included two different compounds. The heavy oxygen-ether in the distillate obtained by heating alcohol with manganese and sulphuric acid was found by Gay-Lussac & Liebig to be oil of wine; while that contained in the liquid produced by the slow combustion of alcohol in contact with platinum-black, was recognized by Döbereiner as a peculiar body, more closely investigated in 1833 by Liebig who gave it the name of acetal, and subjected to a still further examination by Stas, in 1847. — Although Döbereiner did not succeed in obtaining his light oxygen-ether (aldehyde) in a state of purity (vid. Preparation 1), he nevertheless threw out the suggestion that it is alcohol *minus* 2 H; ascribed to it the properties of turning acid by exposure to the air, being charred by oil of vitriol, and converted into a resin when heated with potash; and discovered the crystalline compound which it forms with ammonia. This compound was sent to Liebig who was thereby put in the way of discovering the mode of preparing this compound — to which he gave the name of *Aldehyde* — in the pure state, of examining its chemical relations more minutely, and

determining its composition. To Döbereiner is therefore justly due the honour of discovering this interesting compound, and to Liebig (*Ann. Pharm.* 22, 273) that of its more exact investigation.

Formation. — In many decompositions of alcohol, especially by oxidizing agents and by chlorine; — *e. g.*, in the slow and imperfect combustion of alcohol in the air (pp. 206–211), in its decomposition by chlorine (p. 211), by nitric acid (p. 217), by chromic acid (p. 243), and by sulphuric acid with peroxide of manganese (p. 244), or uranic oxide (p. 245). — 2. In the decomposition of ether by a red heat, and in the slow combustion of ether (pp. 177–179). — 3. In the decomposition of acetic ether, and probably also of other vinic ethers by a mixture of chromic and sulphuric acid. — 4. When hemp-oil is passed through a gun-barrel at a low red-heat, a product is obtained resembling lampic acid, together with a large quantity of aldehyde. (Hess, *Pogg.* 38, 380.) — 5. Wood-vinegar obtained by the dry distillation of wood contains, besides wood-spirit, &c., a much more volatile product (Scanlan), which is aldehyde. (Kane, *Ann. Pharm.* 19, 288.)

¶ 6. In the decomposition of lactic acid (hydrated or anhydrous) and of lactates with weak bases by dry distillation: thus, anhydrous lactate of copper heated to a temperature between 200° and 210°, yields carbonic acid and a distillate containing aldehyde and a small quantity of hydrated lactic acid (probably arising from a trace of water remaining in the salt.) Lactates with strong bases, such as potash, yield different products. (Engelhardt, *Ann. Pharm.* 70, 241.) — 7. In the decomposition of animal casein, albumin, fibrin, and gelatin, by sulphuric acid and peroxide of manganese or bichromate of potash (Guckelberger, vii. 127, 131); also of vegetable fibrin by sulphuric acid and peroxide of manganese. (F. Keller, *Ann. Pharm.* 70, 24.) ¶

Preparation. — 1. Döbereiner (*Schw.* 64, 466; *Pogg.* 24, 603) obtained aldehyde (his light oxygen-ether) in an impure state in the following manner: Alcohol of the strength of 70 per cent. is exposed in the acetic acid lamp (p. 207), to the action of the air and of platinum-black till it begins to expel carbonic acid from chalk, then neutralized by chalk or carbonate of soda and distilled; the distillate is then saturated with chloride of calcium, and the ethereal stratum which floats on the top of the chloride of calcium solution distilled [fractionally?].

The light oxygen ether thus obtained is a hydrated, very mobile liquid, of sp. gr. 0·842, boiling at 75°, neutral, and having a powerful odour like that of *Spiritus Nitri dulcis.* It appears to be $C^4H^4O^2$, and its formation apparently precedes that of acetic acid, into which it is also converted by contact with air and platinum-black, or in the state of aqueous solution, by mere contact with the air. It burns with a white flame. It is quickly converted by oil of vitriol, more slowly by alcoholic potash, into a yellow resin which dissolves in ether and alcohol, but not in potash. It mixes with alcohol in all proportions, but requires about 5 parts of water to dissolve it. — More recently Döbereiner (*Ann. Pharm.* 14, 138) discovered that when ammoniacal gas is passed through the above-mentioned stratum of liquid which floats on the chloride of calcium solution (and is a mixture of acetal and aldehyde) the compound of light oxygen-ether (aldehyde) with ammonia is deposited in crystals.

2. Vapour of absolute ether is passed through a red-hot glass tube filled with fragments of glass, thence into a bottle half filled with absolute

ether and kept cold, ammoniacal gas previously freed from water by passing through a tube filled with lime or hydrate of potash, being also admitted from time to time into the bottle. The aldehyde then combines with the ammonia, and separates from the ethereal mixture in crystals, which must be pressed between bibulous paper and then dried in the air; the product obtained by continuing the process for 24 hours amounts to about 30 grammes. (Liebig.)

3. Two parts of 80 per cent. alcohol are mixed with 3 pts. peroxide of manganese, 3 pts. oil of vitriol, and 2 pts. water, and distilled into a receiver kept at a very low temperature. The mixture is gently heated till it begins to froth slightly, and the distillation interrupted as soon as the liquid which passes over begins to redden litmus, which it does when the distillate amounts to 3 pts. The distillate, consisting of aldehyde, alcohol, &c., is mixed with an equal weight of chloride of calcium, and distilled (the receiver being constantly kept very cold), till $1\frac{1}{2}$ pt. has passed over, and this distillate again rectified with an equal weight of chloride of calcium till $\frac{3}{4}$ pt. has passed over. This last portion is anhydrous, but contains alcohol and certain compound ethers as well as aldehyde. To purify it, 1 vol. is mixed with 2 vol. ether, the mixture surrounded with cold water, and dry ammoniacal gas passed into it to saturation; the gas s absorbed rapidly and with great evolution of heat, and the aldehyde separates out in crystals of aldehyde-ammonia. These crystals are washed three times with absolute ether and dried as above. (Liebig.)

4. A mixture of 1 pt. 80 per cent. alcohol and 2 pts. water is saturated with chlorine gas, (being kept cool all the while) and the liquid distilled, as soon as it has lost the odour of chlorine, till $\frac{1}{20}$ has passed over. That which distils over afterwards is alcohol, which may be collected in a separate receiver and again treated with chlorine as above. The first distillate is again freed from water by repeated distillation, so far as to admit of its being saturated with ammonia as above, and yielding a very large crop of crystals. (Liebig.)

5. Three parts of 80 per cent. alcohol are distilled with 2 pts. of nitric acid of sp. gr. 1·25, and the product rectified over the water-bath. The rectified product, consisting chiefly of nitrous ether and aldehyde, separates when saturated with ammoniacal gas, into two layers, the upper of which is nitrous ether, and the lower a concentrated aqueous solution of aldehyde-ammonia. (Liebig.)

6. One part of alcohol of sp. gr. 0·842 and 1 pt. of bichromate of potash are introduced into a capacious tubulated retort, and $1\frac{1}{3}$ pt. oil of vitriol admitted by drops through the tubulus. The heat evolved by the chemical action which ensues is sufficient to begin the distillation, but towards the end heat must be applied from without. A large quantity of carbonic acid gas is evolved, and the aldehyde condenses in the strongly cooled receiver (Liebig) contaminated with only a small quantity of acetic acid and other substances, so that the distillate may be immediately mixed with ether, and ammoniacal gas passed through it. (W. & R. Rodgers, *J. pr. Chem.* 40, 248.) Engelhardt recommends the dry distillation of lactates with weak bases as a means of obtaining aldehyde. (*comp.* p. 275.)

To obtain the pure aldehyde from the aldehyde-ammonia formed by either of these processes, a solution of 2 pts. of the aldehyde-ammonia in 2 pts. water is distilled in a water-bath at a gentle but increasing heat, with a mixture of 3 pts. oil of vitriol and 4 pts. water, and the distillation interrupted as soon as the water in the bath begins to boil. The receiver *must be* kept as cold as possible. The hydrated aldehyde which passes

white precipitates with mercurous and mercuric salts, the former easily reduced to the metallic state by heat, the latter remaining white even after boiling. (Weidenbusch, *Ann. Pharm.* 66, 155; *Jahresber.* 1847-8, 548.) ¶.

7. *Oxide of silver* heated with aqueous aldehyde, first gently, then slowly to the boiling point, is partially reduced to the metallic state, the metal forming a specular coating on the glass — a proof that no evolution of gas takes place. The liquid contains in solution a silver-salt, which, however, is decomposed by evaporation, the silver being reduced to the metallic state. If it be saturated in the cold with baryta-water and then heated to the boiling point, the precipitated oxide of silver is reduced, and acetate of baryta remains in solution. (Liebig.) — From these experiments, Liebig infers the existence of an *Aldehydic acid*, $C^4H^4O^3$ (or in the hypothetically anhydrous state, $C^4H^3O^2$), intermediate between aldehyde and acetic acid. The liquid obtained by heating oxide of silver with aqueous aldehyde is supposed to contain aldehydate of silver, which is resolved by evaporation into silver and acetic acid; when the oxide of silver is precipitated by baryta-water, aldehydate of baryta is formed, and this when boiled is converted into acetate, while the precipitated oxide of silver is reduced. Liebig supposes also that this aldehydic acid exists in lampic acid (p. 181), and in the distillate obtained by treating alcohol with peroxide of manganese and dilute sulphuric acid. [Since the water, when heated, may still retain a portion of aldehyde, and since the reduction of silver by aldehyde goes on but slowly, it may likewise be supposed that when aqueous aldehyde is heated with oxide of silver, acetate of silver is formed from the very beginning of the action, and that, on further heating this salt either with or without baryta, the silver is reduced by the aldehyde still remaining in the liquid. At all events, from the point of view of the nucleus-theory, the existence of an acid with 3 At. oxygen is highly improbable]. — Silvering of the glass is also produced on heating aqueous aldehyde with solution of nitrate of silver and a few drops of ammonia. — This is the best mode of detecting small quantities of aldehyde in other liquids, such as nitrous ether and heavy hydrochloric ether. (Liebig.) Aldehyde-ammonia dissolved in water likewise reduces oxide and nitrate of silver when heated with them. (Liebig.) The latter reduction takes place at 0° in 2 or 3 minutes; the solution of 1 pt. nitrate of silver in 1000 pts. water forms when heated with aldehyde, a shining metallic mirror; with 1 pt. of the salt in 2000 pts. water, the mirror is formed only here and there on isolated spots, the liquid assuming a purple-green colour [(?) violet arising from metallic silver. VI. 137]; when the quantity of water is increased to 10,000 parts, no mirror is formed, but the liquid, after being heated for three minutes, assumes a dark red-green colour; even a solution containing only 1 pt. of the silver-salt in 40,000 pts. water, in which chloride of sodium produces only a slight opalescence, still exhibits distinct colouring with aldehyde. (W. & H. Rogers, *J. pr. Chem.*)

8. Aldehyde heated with alcoholic *Potash* is converted into a yellow resin. (Döbereiner.) Even when aqueous aldehyde is heated with potash and the air excluded, a yellowish turbidity is produced, and subsequently *Aldehyde-resin* separates out, from below upwards, in the form of a reddish brown substance which may be drawn out into threads. The alkaline liquid contains a small quantity of an organic acid, whose potash-salt turns brown when its aqueous solution is evaporated; this acid heated with salts of silver or mercury reduces them without effervescence.

(Liebig.) — ¶ According to Weidenbusch, aldehyde-resin is a substance of a fiery orange-yellow colour, which, when dried at 100°, is reduced to a powder having a paler colour. It dissolves in alcohol and ether, sparingly in water, scarcely at all in alkalis, partially in strong sulphuric acid; from the latter solution it is re-precipitated by water. Its alcoholic solution is rapidly decolorized by chlorine, and when subsequently mixed with water, yields a snow-white powder still containing chlorine. The resin, purified as completely as possible, was found to contain 76·4 p. c. carbon, and 8·0 p. c. hydrogen; its formation is accompanied by that of acetic, formic, and aldehydic (acetylous) acid, which unite with the alkali; at the same time a pungent odour is evolved, proceeding from a peculiar substance which adheres obstinately to the resin, and cannot be completely separated from it; the substance is oily and volatile when first produced, but soon thickens, even when alone, and still more quickly under the influence of nitric acid, and is converted into a golden-yellow, viscid resin, which smells like cinnamon, dissolves in alcohol and ether and sparingly in water, and is different from the true aldehyde-resin. (*Ann. Pharm.* 66, 153, *Jahresber.* 1847–8, 548.) ¶ — 9. When vapour of aldehyde is passed through a hot tube filled with a mixture of *lime and hydrate of potash*, the mixture suddenly turns brown, then becomes decolorized and gives off a large quantity of hydrogen, and is afterwards found to contain acetate of potash without any formiate:

$$C^4H^4O^2 + HO,KO = C^4H^3KO^4 + 2H.$$

(Dumas & Stas, *Ann. Chim. Phys.* 73, 151; also *Ann. Pharm.* 35, 161; also *J. pr. Chem.* 21, 273.) — 10. Potassium introduced into aldehyde, even if the liquid be cooled, causes such violent ebullition, though without perceptible evolution of heat, that the aldehyde quickly evaporates. Vapour of aldehyde passed over potassium immediately gives off hydrogen gas. (Löwig, *Pogg.* 43, 623.) Anhydrous aldehyde forms with potassium and sodium, compounds consisting of hypothetically anhydrous aldehyde with the alkali. (Liebig, *Ann. Pharm.* 25, 17):

$$C^4H^4O^2 + K = C^4H^3KO^2 + H, \text{ or } = KO,C^4H^3O + H.$$

11. *Cyanic acid* vapour evolved from heated cyanuric acid, is quietly absorbed by anhydrous aldehyde at 0°; but even at ordinary temperatures the mixture becomes heated, continuously gives off carbonic acid gas, ultimately froths up, and solidifies into a mass like burnt borax, consisting of *Trigenic acid*, $C^6N^3H^7O^4$, together with small quantities of cyamelide, aldehyde-ammonia, and perhaps also other products. (Liebig & Wöhler, *Ann. Pharm.* 59, 296):

$$C^4H^4O^2 + 3C^2NHO^2 = C^6N^3H^7O^4 + 2CO^2.$$

¶ 11. When *Hydrosulphuric acid gas* is passed for some time into a mixture of aldehyde and water, the liquid becomes turbid and deposits a viscid, transparent and colourless oil, which has a disagreeable alliaceous odour, and when dried in vacuo has a density of 1·134; its composition is $C^{12}H^{13}O^7$, and its formation is represented by the equation:

$$3C^4H^4O^2 + 7HS = C^{12}H^{13}O^7 + 6HO.$$

(Weidenbusch, *Ann. Pharm.* 66, 158.) ¶

12. In contact with *Ammonia* and *Hydrosulphuric acid* together, aldehyde yields *Thialdine* and water.

$$3C^4H^4O^2 + NH^3 + 4HS = C^{12}NH^{13}S^4 + 6HO.$$

Similarly, *Hydroselenic* acid produces *Selenaldine* (q. v). (Liebig & Wöhler, *Ann. Pharm.* 66, 1.)

Combinations. Aldehyde mixes in all proportions with water, the mixing being attended with rise of temperature. A mixture of 1 pt. aldehyde and 3 pts. water boils at 37°. Chloride of calcium added to the aqueous solution separates the aldehyde in the form of a clear liquid which rises to the surface.

Aldehyde dissolves *Phosphorus* and *Sulphur*, — also *Iodine*, forming a brown solution and without decomposition. (Liebig.)

Aldehyde-Ammonia. $NH^3,C^4H^4O^2$. — Ammoniacal gas passed into pure aldehyde combines with it, giving off heat and forming a white crystalline mass. If the aldehyde be previously mixed with ether, the compound separates in distinct crystals; the finest are obtained by mixing a concentrated alcoholic solution of aldehyde-ammonia with ether. (Liebig.) — Acute rhombohedrons with terminal edges of about 85°, often truncated with faces of another rhombohedron. (G. Rose.) Transparent, colourless, shining, strongly refractive, of the hardness of common sugar, and very friable. Melts between 70° and 80°, and distils unaltered at 100°. In the state of vapour and in aqueous solution, it reddens turmeric paper. Its odour is ammoniacal, but has likewise the character of turpentine. (Liebig.)

			Liebig.
4 C	24	39·34	39·78
N	14	22·95	23·00
7 H	7	11·48	11·45
2 O	16	26·23	25·77
$NH^3,C^4H^4O^2$	61	100·00	100·00

Aldehyde-ammonia is very inflammable. In contact with the air, especially if also exposed to light, it becomes yellow [brown and unctuous], and acquires an odour resembling that of burnt animal substances. By distillation it may again be obtained in the colourless state, and leaves a brown residue, which is soluble in water and contains acetate of ammonia and another ammoniacal salt. Even the weaker acids, such as acetic acid, separate the aldehyde from the compound. Oil of vitriol and potash act upon it in the same manner as upon aldehyde. Its aqueous solution, digested with oxide of silver, reduces part of this oxide and dissolves the rest, forming an aldehydate [or acetate ?] of silver mixed with ammonia, from which the oxide of silver is precipitated by baryta-water, and reduced when the liquid is heated, while acetate of baryta remains in solution. — Aldehyde-ammonia dissolves with very great facility in water, less easily in alcohol, and not at all in ether. (Liebig.)

Silver-compound. The concentrated aqueous solutions of aldehyde-ammonia and nitrate of silver yield, when mixed, a very fine-grained, white precipitate, which may be purified by washing with alcohol. It

contains nitric acid, ammonia, oxide of silver, and aldehyde, viz., 41·78 p. c. (1 At.) silver, 19·04 p. c. (8 At.) C, and 4·21 p. c. (11 At.) H. — It dissolves very sparingly in alcohol, easily in water. When the aqueous solution is heated to the boiling point, aldehyde is given off, half the silver reduced; and the remaining liquid, which has no acid reaction, contains nitrate of ammonia and aldehydate of silver, consequently gives off ammonia when heated with potash, and nitrous fumes when heated with oil of vitriol. (Liebig.)

Aldehyde mixes in all proportions with *Alcohol and Ether*, producing rise of temperature. (Liebig.)

Three Compounds isomeric with Aldehyde.

Liebig (*Ann. Pharm.* 14, 141; *Chemische Briefe*, 154) discovered the liquid and the infusible solid compound; Fehling (*Ann. Pharm.* 27, 319), the fusible solid compound.

A. *Liquid.* — Pure aldehyde sealed up in a tube, changes in the course of a few days or weeks into a liquid, which has a pleasant ethereal odour, boils at about 81°, and no longer forms a resin with potash; it may be exposed to the air without oxidizing and changing into acetic acid, and does not mix with water, but floats upon it. (Liebig, *Chem. Br.*)

B. *Solid and fusible. Elaldehyde.* Anhydrous aldehyde enclosed in a tube, together with pieces of chloride of calcium, for two months in winter, yielded long transparent prisms, which however disappeared again after a fortnight, so completely that not a trace of them could be perceived in the liquid. — These crystals melt at +2°, solidify at 0°, and boil at 94°, giving off a vapour whose density is 4·5157. In the fused state this substance has an ethereal odour, more agreeable and less pungent than that of aldehyde; its taste is somewhat burning. It burns with a blue flame; its vapour passed through a red-hot tube, yields a combustible gaseous mixture, and a small quantity of a liquid having an empyreumatic odour. Oil of vitriol blackens the crystals slowly in the cold, immediately when heated. The crystals may be heated with potash-ley for some time without becoming coloured, and solidify again on the surface as the liquid cools. When heated with aqueous nitrate of silver, they throw down the silver in the form of a grey powder, not of a specular coating. When dissolved in ether, they do not absorb ammoniacal gas, but remain unaltered. (Fehling.)

C. *Solid and infusible. Metaldehyde.* Anhydrous aldehyde kept for some time in a sealed tube or well stoppered bottle, frequently deposits transparent, colourless, four-sided prisms, which traverse the whole liquid like a network. The crystals remain solid at 100°, but at a stronger heat sublime undecomposed, in the form of transparent, colourless, shining, rather hard needles, which are easily pulverized, inodorous, combustible, scarcely at all soluble in water, but easily soluble in alcohol and ether. (Liebig.) — Fehling, by exposing pure aldehyde to the cold of winter for several weeks, once obtained the same crystals, mixed, however, with a larger quantity of the crystals B. They are hard and easy to pulverize;

at 120°, they sublime without previous fusion. When they are suffered to evaporate in the air, the vapour condenses in fine snowy flakes.

	Fehling. *Compound* B.	Fehling. *Compound* C.
C	54·55	54·51
H	9·16	9·05
O	36·29	36·44
	100·00	100·00

Liebig supposes that the oxidation which takes place when aldehyde is exposed to the air, may produce a disturbance of equilibrium and an internal motion of the atoms, which continues after the air is excluded and causes the atoms to arrange themselves in a new order, so as to form one or other of these isomeric compounds.

[The liquid compound A is perhaps acetic ether, $C^8H^8O^4$; the fusible compound B might, from its vapour-density, which is three times as great as that of aldehyde, be regarded as $C^{12}H^{12}O^6$, although its boiling point is rather in favour of the formula $C^8H^8O^4$; the compound C may be $C^{16}H^{16}O^8$ or $C^{12}H^{12}O^6$].

Acetic Acid. C^4H^4,O^4.

WESTENDORFF. *Diss. de opt. acet. conc.* &c. Gott. 1772.
BERTHOLLET. *Mém.* Par. 1783, 403; also *Crell. Ann.* 1789, 1, 536.
LOWITZ. *Crell. Ann.* 1786, 1, 255; 1789, 2, 584; 1799, 1, 206; 1793, 1, 219.—*Scher. J.* 3, 600.
CHAPTAL. *Scher. J.* 2, 102.
ADET. *Scher. J.* 2, 170.
DABIT. *Ann. Chim.* 38, 66; also *Scher. J.* 8, 135.
DARRACQ. *Ann. Chim.* 41; also *Scher. J.* 9, 615.
PROUST. *J. Phys.* 56, 210; *Ann. Chim.* 61, 111.
TROMMSDORFF. *A. Gehl.* 5, 573.
RICHTER. *Neuere Gegenst.* 6, 5.
CHENEVIX. *Ann. Chim.* 69, 5; also *Gilb.* 32, 156.
MOLLERAT. *Ann. Chim.* 68, 88.
BERZELIUS. *Ann. Chim.* 91, 301.—Copper-salts. *Pogg.* 2, 233.
SÉBILLE-AUGER. *J. Chim. méd.* 8, 233.

Essigsäure, Acetylsäure, Acide acétique.—In the most concentrated state it is also called *Glacial Acetic acid, Eisessig, Radicalessig, Acetum radicale, Alcohol aceti, Acidum aceti crystallisatum, Sel de Vinaigre*; and when distilled from verdigris: *Spirit of Copper, Kupferspiritus, Spiritus Æruginis* s. *Veneris.*

Vinegar is mentioned by Moses; the alchemists were acquainted with *spiritus æruginis.* The statement put forward by Berthollet and adopted by Chaptal and Dabit, that the acetic acid obtained from verdigris is richer in oxygen than ordinary acetic acid—whence they distinguished it by the name of acet*ic* acid from the common or acet*ous* acid—was disproved especially by Adet and Darracq. Trommsdorff also showed the incorrectness of Proust's statement, that acetic acid contains nitrogen.—

Fourcroy & Vauquelin (*Scher. J.* 5, 268), showed that the so-called *pyromucic acid* (*brenzliche Schleimsäure*) obtained by the dry distillation of sugar, manna, honey, gum, and starch, and the pyroligneous acid (*brenzliche Holzsäure*) produced by the dry distillation of wood, which were formerly regarded as peculiar acids, are merely acetic acid contaminated with empyreumatic oil. — Thénard showed (*Ann. Chim.* 43, 176; also *Scher. J.* 10, 637), that the *zoonic acid*, which Berthollet (*Ann. Chim.* 26, 86; also *Scher. J.* 1, 197) obtained by the dry distillation of animal substances, and regarded as a peculiar acid, was in reality a mixture of acetic acid with another substance which imparted to it the property of precipitating nitrate of lead and mercurous acetate.

Sources. Acetic acid occurs, sometimes free, sometimes associated with potash and lime, in the juice of many plants, especially of trees; in small quantities in certain animal fluids; and according to A. Vogel (*J. Pharm.* 12, 8), in certain mineral waters.

Formation. 1. By the dry distillation of most non-volatile organic compounds; by passing volatile organic compounds through red-hot tubes; and by the imperfect combustion of most organic bodies. — The acetic acid which passes over during the dry distillation of non-azotized organic compounds, is contaminated with empyreumatic oils and resins, and that which is evolved from azotized organic bodies is more or less saturated with ammonia and volatile alkaloids. (VII, 78–81.) — *Wood-vinegar, Pyroligneous acid, Holzessig, brenzliche Scheimsäure, Zoonische Säure.*

2. By the slow combustion and spontaneous decomposition of many organic compounds. — Platinum-black converts olefiant gas mixed with oxygen into acetic acid (p. 166); aldehyde is converted into acetic acid by simple exposure to the air, and alcohol when exposed in contact with finely divided platinum (p. 207), or with an alkali (254), or when placed in a state of dilution in contact with air and certain organic matters. (vid. *Acetous Fermentation.*) — *Wine-, Beer-, Cider-,* and *Brandy-vinegar.* In this case, the alcohol is first converted into aldehyde, and then into acetic acid. (Liebig.) — Also sugar, starch, and certain other substances, which contain no alcohol, at least ready formed, produce a certain quantity of acetic acid when they undergo spontaneous decomposition in contact with certain other substances.

3. Nitric acid, chromic acid, a mixture of manganese and sulphuric acid, &c., form with many organic compounds, such as alcohol, sugar, starch, oleic acid, gelatin, &c., a number of products among which is acetic acid. Many organic compounds, sugar and starch for example, likewise yield a small quantity of acetic acid when heated with oil of vitriol.

4. Acetic acid is also formed when alcohol (p. 254), tartaric acid, mucic acid, malic acid, succinic acid, citric acid, sugar, *Semen Lycopodii*, &c., are strongly heated with hydrate of potash. (*comp.* VII, 135.)

¶ 5. By the action of aqueous solution of potash on cyanide of methyl (Frankland & Kolbe, *Ann. Pharm.* 65, 288; Dumas, Malaguti & Leblanc, *Compt. rend.* 20, 474.) ¶

Matteucci (*Ann. Chim. Phys.* 52, 134; abstr. *Pogg.* 31, 32) states that he has obtained acetic acid from inorganic materials, viz., by passing carbonic oxide gas into water containing finely divided copper, the product being a blue solution of acetate of copper. Berzelius (*Jahresber.* 13, 223) did not succeed with this experiment. Matteucci used the finely

divided copper obtained either by reducing the oxide by hydrogen, or by the distillation of verdigris; the latter perhaps contained some undecomposed basic acetate of copper.

For this formation of acetic acid from bisulphide of carbon, *vid.* VII, 41.

Preparation of Hydrated Acetic Acid. — 1. By *Fermentation.* *a. Crude Vinegar, Acetum crudum. Wine-, Cider-, Beer-,* and *Brandy-vinegar.* Obtained when wine, cider, beer, or dilute alcohol is exposed for some time to the air, under favourable circumstances. Crude vinegar contains, besides acetic acid, a large quantity of water, frequently also undecomposed alcohol, cream of tartar and other salts, gum, colouring matter, tannin, ferment, &c. — Respecting the adulteration of vinegar with sulphuric, hydrochloric, nitric, tartaric acid, and acid vegetable matters, *comp.* Pleischl (*Zeitschr. Phys. Math.* 10, 257); — Kühn. (*Schw.* 59, 371); — Runze (*Pogg.* 31, 518); — Payen (*N. Ann. Sc. Nat. Bot.* 10, 222); — Orfila (*J. Chim. méd.* 17, 473). — *N. J. Pharm.* 11, 10); — Guibourt (*N. J. Pharm.* 10, 407; 11, 91); — Wislin (*J. Pharm.* 54, 252); — Pettenkofer (*Repert.* 83, 87); — Chevalier (*J. Chim. méd.* 22, 772; 23, 395).

b. Distilled Vinegar, Acetum destillatum. Obtained by distilling crude vinegar, as far as it can be done without burning the residue, in metallic, or better in glass vessels. At first the most dilute acid passes over, together with any alcohol that may be present; the subsequent portions of the distillate continually increase in strength, and the residue contains the strongest acid. Hence distilled vinegar is weaker than the crude. — A portion of the acid retained in the residue may be obtained, in a very weak state however, by diluting the residue several times with water and distilling. If the distillate still contains a small quantity of alcohol, it causes platinum-black moistened with it to swell up, with formation of bubbles. (Döbereiner, *Schw.* 63, 478.)

c. Concentrated Vinegar, Acetum concentratum. — *a.* Obtained by uniting distilled vinegar with potash, soda, lime, or oxide of lead, evaporating till the acetate remains, either in the state of concentrated solution, or of crystals, or of a dry mass, and distilling the residue with more or less of dilute sulphuric acid. — On the small scale the distillation is conducted in glass retorts, on the large scale, in stills of lead or copper fitted with head and condensing tube of tin, stone-ware, or glass. The most advantageous material for the purpose is the acetate of lead (sugar of lead), prepared on the large scale. 190 pts. (1 At.) of the crystallized salt required 49 pts. (1 At.) oil of vitriol, diluted with two or more times its weight of water. It is well to let the materials act upon each other at a gentle heat for a few days before distilling, so that all the acetate of lead may be previously converted into sulphate, and no sulphuric acid may be present at the commencement of the distillation; because that acid would then be converted into sulphurous acid, which would pass over and contaminate the distillate. (Geiger.) Some manufacturers add to the mixture a certain quantity of pulverized peroxide of manganese, to convert the sulphurous acid into sulphate of manganese. This method, however, is not so good as the preceding; for the manganese coming in contact with the free sulphuric acid may likewise decompose part of the acetic acid by oxidation; moreover the manganese gives rise to percussive ebullition. — Whichever method is adopted, the receiver should be changed towards the end of the distillation, because the last portions

are very likely to be contaminated with sulphurous acid and empyreumatic products.

If it be not desired to obtain a concentrated acid, a solution of 190 pts. sugar of lead in twice that quantity of boiling water may be precipitated by 49 pts. oil of vitriol diluted with its own or a double quantity of water, the liquid decanted from the precipitated sulphate of lead, or strained and pressed through linen, and distilled alone. In this case, the distillation goes on much more easily, and there is but little chance of contamination with sulphurous acid or empyreumatic products. A further portion of very dilute acid may be obtained by washing the sulphate of lead and distilling the wash-water. (Runzler, *Br. Arch.* 3, 393; 8, 82; Anthon, *Repert.* 81, 240.)

β. Distilled vinegar is exposed to a very low temperature, so that the water may separate from it by congelation; the concentrated vinegar suffered to run off; and the same treatment repeated several times, a lower temperature being employed at each repetition.

γ. Distilled vinegar is re-distilled over charcoal powder; the very weak acid which first passes over received alone; and the concentrated acid which goes over afterwards collected in a separate receiver. (Löwitz.)

2. *By the combustion of Alcohol in contact with Platinum-black.* A large glass case having a gable top, contains a number of shallow vessels of glass, porcelain, or wood, so arranged as to be distant about four inches from each other and from the bottom. Each of these vessels is covered with a layer of platinum-black, a line in thickness, moistened with water, and on the floor of the glass case is placed as much strong spirit or brandy as can be oxidized by the air within the case. The whole is exposed to ordinary daylight or sunshine, the temperature kept at 20° to 30°, and evaporation of the alcohol promoted by hanging up a few sheets of bibulous paper so that they may dip into it. Oxidation then begins in a few minutes; the platinum-black becomes heated; the acetic acid condenses on the glass sides of the case; and in the course of 8 to 12 hours, the alcohol is completely converted into acetic acid, which, after the apparatus has cooled and the air been renewed, may be replaced by fresh alcohol. In this manner, with a glass case of the capacity of 12 cubic feet, and by the use of 6 oz. of platinum-black, 1 pound of absolute alcohol, or 3 pounds of brandy may be converted into acetic acid in a day. (Döbereiner, *Schw.* 63, 235). But the acid thus obtained is contaminated with aldehyde and acetal (p. 207.)

3. *By the dry distillation of Wood.*—Channels are formed in the lower part of the charcoal-kiln (*Kohlenmeiler*), through which the condensed vapours of the imperfectly burning wood may run off; or wood is placed in an iron vessel and heated by fire applied from without till it chars; or wood contained in a still built up in brickwork is heated by furnaces till it is converted into charcoal, and the evolved vapours condensed.

The *Wood-Vinegar* thus obtained, which requires to be separated from wood-tar, is treated by Mollerat (*Ann. Chim. Phys.* 12, 205) as follows: It is rectified, whereby the greater part of the resin and more fixed empyreumatic oil is separated and remains behind; the distillate is saturated with carbonate of potash (or quicklime); sulphate of soda added to precipitate the lime; the solution of acetate of soda separated from the gypsum and evaporated to dryness; the residue exposed to a strong heat sufficient to decompose the empyreumatic por-

tions, but not the acetic acid; the acetate of soda purified by solution in water, filtering, and crystallization; and lastly the purified salt distilled with dilute sulphuric acid. — Pajot-Descharmes (*J. Pharm.* 4, 327) saturates the rectified wood-vinegar with milk of lime or carbonate of lime; evaporates the impure acetate of lime to dryness; roasts it on a cast-iron plate till it chars; redissolves it in water; precipitates the lime by sulphuric acid; and distils the liquid after decanting it from the gypsum. — Prückner (*J. pr. Chem.* 4. 21) proceeds in the same manner, excepting that, after roasting the acetate of lime and re-dissolving it in water, he immediately distils it with sulphuric acid in a cast-iron vessel. — According to Stoltze (*Anleitung die rohe Holzsäure zu reinigen und zu benutzen*, u. s. w. Halle and Berlin, 1820), charcoal-powder removes from wood-vinegar only the more strongly resined oil, and consequently the colour, but not the pungent taste and odour. He purifies it by distillation, continuing the process as long as the acid passes over colourless, and by digesting the distillate with peroxide of manganese, or with oil of vitriol, or with a mixture of manganese and oil of vitriol, or with manganese, common salt and oil of vitriol (whereupon, by the action of oxygen, sulphuric acid, or chlorine, the empyreumatic oil is further resinized, and thereby rendered more easy of absorption by the charcoal), and by a second distillation over charcoal. Concentrated vinegar prepared from wood-vinegar often has but a very slight empyreumatic odour, but immediately acquires a dark colour on being mixed with oil of vitriol. (Stockhardt, *N. Br. Arch.* 38, 15). — ¶ Völckel (*Ann. Pharm.* 82, 49; abst. *Chem. Soc. Qu. J.* 5, 274) saturates the crude wood-vinegar with lime, whereupon part of the resinous impurities separate out; evaporates the clarified liquid to half its bulk; then adds hydrochloric acid in sufficient quantity to produce a decided acid reaction after cooling (from 4 to 6 pounds of acid to 150 litres or 33 gallons of the wood-vinegar), which causes the dissolved resins to separate and rise to the top of the liquid, so that they may be easily skimmed off, and likewise decomposes the lime-compounds of creosote and other volatile substances, which may then be expelled by further evaporation. He then further evaporates the solution, and carefully dries the residue on cast-iron plates till it becomes nearly or quite inodorous; when thoroughly dried, it has a dirty brown colour. To obtain the acid from this purified acetate of lime, it is distilled with hydrochloric acid (from 90 to 95 parts of hydrochloric acid of 20° B. or sp. gr. 1·16 to 100 pts. acetate of lime). The salt dissolves in the hydrochloric acid, forming a dark-coloured liquid from which a quantity of resin separates. As the whole mass is liquid, the heat diffuses through it easily; and as the acetic acid passes over between 100° and 120°, and the acetate of lime has already been exposed to a drying temperature, the distilled acid is but very slightly contaminated with empyreumatic products. It is also perfectly colourless, and if the hydrochloric acid has not been added in excess, gives but a slight cloud with nitrate of silver. The resin should be skimmed off as much as possible before distillation, to prevent spirting. The acid obtained by this process has a sp. gr. of 1·058 to 1·061, equivalent to 20° B. As, however, acetic acid of this degree of concentration is rarely required, and a somewhat weaker acid may be distilled off with greater facility, it is better to add a certain quantity of water either before or towards the end of the distillation. A good proportion is: 100 pts. acetate of lime, 90 to 95 pts. hydrochloric acid, and 25 water; this gives from 95 to 100 pts. of acetic acid of 7° B., or sp. gr. 1·105. In this manner, 150 litres of wood-vinegar yield 60 lbs. of acetic

acid of this strength. The acid thus obtained may be still further purified by mixing it with a small quantity of carbonate of soda and distilling again. The acid which passes over is perfectly colourless, and free from hydrochloric acid, but still retains a slight empyreumatic odour. But even this may be removed by distilling it with 2 or 3 per cent. of bichromate of potash instead of carbonate of soda. — The use of hydrochloric acid instead of sulphuric in the decomposition of the acetate of lime, has this great advantage, that the presence of resins, colouring matter, &c. does no harm, provided the acetate has been sufficiently heated to drive off all free volatile substances. When, on the contrary, sulphuric acid is used, the acetic acid always has a bad odour, is saturated with sulphurous acid, and contaminated by various products arising from the decomposition of the resins at a high temperature. Moreover, the sulphate of lime forms a hard crust at the bottom of the still; the last portions of acid are often turbid from the presence of separated sulphur; and the odour of sulphuretted hydrogen becomes perceptible, in consequence of the reduction of the sulphate of lime to sulphide of calcium at the bottom of the vessel; from this cause, cast-iron stills soon become corroded. — The same process may also be applied to the preparation of pure acetic acid from brandy-vinegar. As, however, the acetate of lime formed with the latter is less contaminated with foreign matter than that formed from wood-vinegar, a larger proportion of hydrochloric acid is required to decompose it, viz. about 130 pts. of acid to 100 pts. of the lime-salt. ¶

Preparation of Glacial Acetic Acid. 1. An intimate mixture of at least 49 pts. oil of vitriol and 98 pts. dry pulverized acetate of potash, or 82 dry acetate of soda, or 79 dry acetate of lime, or 163 dry acetate of lead, is distilled at a very gentle heat:

$$C^4H^3KO^4 + HO,SO^3 = C^4H^4O^4 + KO,SO^3.$$

The 49 pts. oil of vitriol may be replaced by 136 pts., or rather by a considerably larger quantity, of fused and finely pounded bisulphate of potash, which must be mixed as intimately as possible with the acetate:

$$C^4H^3KO^4 + KO,HO,2SO^3 = C^4H^4O^4 + 2(KO,SO^3).$$

The four acetates must be dried by exposure to a gradually increasing heat, and stirred all the while. As, however, the acetate of lead may by this treatment be deprived of a considerable quantity of acetic acid, Berzelius recommends that it be dried by placing it in the state of powder in vacuo over oil of vitriol for 36 hours, or exposing it to the air for a longer time at 30° or 40°, and afterwards heated in the air for an hour to 100°, at which temperature no fusion takes place. Mitscherlich, on the contrary (*Lehrb.* 2, 134), heats the acetate of lead gently and continuously, stirring constantly till it is converted into a dry powder. — The oil of vitriol must be previously freed from excess of water by boiling. (Berzelius.)

Stahl distilled 1 pt. oil of vitriol with 2 pts. acetate of potash; Westendorf, with 2 pts. acetate of soda; Lowitz, with $\frac{3}{4}$ pt. acetate of soda. — To 3 pts. acetate of soda, Lowitz also recommends 8 pts. bisulphate of potash.

With acetate of soda a large excess of oil of vitriol is required, *viz.* 101 pts. oil of vitriol to 82 pts. acetate of soda; otherwise only part of the acetic acid is separated, and the distillate is contaminated with sul-

phurous acid and acetone. The heat which the oil of vitriol produces with the acetate of soda is sufficient to drive over $\frac{1}{4}$ of the acetic acid, without any application of heat from without. The mixture is then gradually heated over an open fire; the distillation is complete by the time the whole mass is fused. A weaker acid passes over at first, and afterwards the strongest acid, having a density of 1·062 at 16°. The distillate amounts to $\frac{2}{3}$ of the acetate of soda. If the oil of vitriol contains nitric acid, red fumes pass over at first; these however do no harm, as they are not absorbed by the acetic acid. (Sébille-Auger.)

With acetate of lead no excess of oil of vitriol is required; a slight excess of the latter gives rise to the formation of sulphurous acid, but prevents that of acetone.

Acetate of lead well dried and pulverized is introduced into a tubulated retort or into a glass or earthen still, and oil of vitriol added in successive portions, the vessel being well cooled from without by cold water to prevent the mass from getting too hot; the mixture is then well stirred with a glass rod, or according to Mohr's recommendation, it is left to itself for 24 hours, so that the oil of vitriol may diffuse itself uniformly through the powders. The retort is connected with a dry receiver, — or the flask, by means of a cork or a caoutchouc joint, with a long tube which first goes upwards and then slowly downwards (*App.* 51) and leads into a simple cooled receiver. The distillation is performed in a bath of strong solution of chloride of calcium, or by very careful heating in the sand-bath.

To obtain glacial acetic acid from sugar of lead by means of bisulphate of potash, HO,SO^3+KO,SO^3, the latter must first be freed from excess of water by heating it till it is brought to a state of tranquil fusion; pulverized very finely after cooling; 137·2 pts. (1 At.), or better an excess of it, very intimately mixed with 163 pts. (1 At.), of dehydrated acetate of lead; and the mixture carefully heated in a distillatory apparatus. In this manner, the acid is obtained in a drier state than by the use of oil of vitriol. (Mitscherlich.) — Brandenburgh took 2 pts. of dry acetic of lead to 5 pts. bisulphate of potash.

2. By distilling acetate of potash alone. — When an excess of acetic acid, not too dilute, is mixed with monoacetate of potash and distilled, a more dilute acid passes over and biacetate of potash remains; and this, when exposed to a heat rising from 200° to 300°, gives off the glacial acetic acid, which may be collected in a separate receiver. The heat must not be suffered to rise above 300°; otherwise a pale rose-coloured distillate will be obtained, containing acetone and empyreumatic oil. The distillate thus obtained is rectified, the first and last portions which pass over being rejected; the middle portion is glacial acetic acid. — The monoacetate of potash in the retort may be repeatedly used for the same purpose. (Melsens, *Compt. rend.* 19, 611; also *J. pr. Chem.* 33, 419.)

3. By distilling crystallized neutral cupric acetate, or a mixture of equal parts of dry acetate of lead and effloresced blue vitriol. (Lauragais): *Spiritus Æruginis* s. *Veneris*. Water passes over first, then tolerably pure glacial acetic acid, mixed, however, towards the end, with a continually increasing quantity of acetone. The distillate obtained in the middle of the process must be freed by rectification from copper mechanically carried over (in the form of cuprous acetate ?).

4. By moistening a large quantity of charcoal-powder in a retort with a *small* quantity of concentrated vinegar, and distilling with a fresh

receiver. — The first portion of the distillate is very weak, the last strong acetic acid. If the latter be redistilled from fresh charcoal-powder, the first portion which passes over is chiefly water, but the subsequent portion consists of a stronger acid, which by repeated fractional distillation may be brought to the state of glacial acetic acid. (Lowitz.)

This process succeeds also without charcoal-powder, inasmuch as even then the weakest acid goes over at the beginning, and the strongest at the end of the distillation. Distilled vinegar or wood-vinegar is brought to a strength of 20 per cent. acid by distillation from effloresced Glauber's salt; this liquid distilled alone to half its bulk; the weak distillate set aside; and the remainder distilled nearly to dryness. The acid thus obtained has already a strength corresponding to 10·656 Bm. at 10°, and yields by fractional distillation a liquid whose density gradually rises to 10·77....11·3 Bm.; by frequently changing the receiver, successive distillates are obtained, continually increasing in strength, and more inclined to deposit crystals of glacial acetic acid by cooling. (Sébille-Auger.)

Impurities in Acetic Acid.

Concentrated vinegar may be contaminated with *sulphurous acid* (proceeding from the decomposition of the excess of sulphuric acid by overheating, and recognizable by its odour, as well as by the method indicated at page 172, vol. II.); with *sulphuric acid;* with *hydrochloric acid* (if the acetate of potash or soda used contained chloride of potassium or sodium); with *nitric acid* (if the oil of vitriol used contained that substance); with *acetate* or *sulphate* of *potash, soda, lime,* or *oxide* of *lead.* — The vinegar may be freed from all these substances by a second distillation with a small quantity of pure acetate of soda; when sulphurous acid is present, however, the vinegar must be previously left for some time in contact with finely pounded peroxide of manganese or lead, till it no longer exhibits the reactions of sulphurous acid.

The same impurities may be present in glacial acetic acid. In this case also the nitric acid may arise from the use of bisulphate of potash obtained as a residue in the preparation of nitric acid, inasmuch as this residue often contains undecomposed nitre. The mode of purification is the same. — Glacial acetic acid may also contain acetone and empyreumatic oil, produced by over heating, these impurities being especially abundant when the acetic acid has been prepared from acetate of copper. These bodies impart to the acid their own peculiar odour. They may, for the most part, be separated by allowing the glacial acetic acid to freeze, and the mother-liquor in which they remain to drop out. — Lastly, the glacial acetic acid may likewise contain excess of water, in which case it will solidify but imperfectly or not at all on exposure to cold, not even if the vessel be opened and shaken. If any portion has solidified, it is separated from that which still remains liquid, and the latter distilled by Sébille-Auger's method, the receiver being frequently changed, because the water passes over chiefly at the beginning of the distillation, the latter portions of the distillate being less and less hydrated. Mohr. (*Ann. Pharm.* 31, 280) distils off $\frac{1}{3}$ of the liquid, and observes whether the residue solidifies at $+4°$ on opening the tubulus of the retort; if this be not the case, he distils off a larger quantity, till solidification takes place. The whole is then left for a few hours, and the liquid portion suffered to run out of the retort; this liquid, if again subjected to partial

distillation, yields an additional quantity of the crystalline product.—Peres (*Scher. J.* 2, 180) proposed to dehydrate acetic acid by distillation with oil of vitriol.

Properties. Glacial acetic acid solidifies below +13° (Lowitz), at 15° (Sébille-Auger) in anhydrous crystalline tables and prisms. In closed vessels, it remains fluid at 12°, and does not crystallize till the vessel is opened and shaken. (Lowitz, I. 10). In the solid state it has a sp. gr. of 1·100 at 8·5° (Persoz, *Ann. Chim. Phys.* 63, 339). The acid melts at +16° (Lowitz), scarcely at +22·5° (Mollerat), to a thin transparent and colourless liquid. The sp. gr. of this liquid is, according to Mollerat, 1·063; according to Persoz, 1·065 at 13°; according to Mohr, 1·0635 at 15°; and according to Sébille-Auger, who appears to have examined the most concentrated and therefore the lightest acid, it is 1·0622 at 16°; according to Kopp (*Pogg.* 72, 1), it is 1·08005 at 0°. It boils at 119° (Sébille-Auger), at 117·3° (Kopp). The tension of its vapour is equivalent to 7·7mm. at 15°, to 14·5mm. at 22°, and 23mm. at 32°. (Bineau, *N. Ann. Chim. Phys.* 18, 226). The vapour-density exhibits the anomaly described at page 54, vol. VII., *viz.*, that for temperatures considerably above the boiling point, it corresponds to that of a diatomic gas, but near the boiling point, to that of a $\frac{2}{3}$-atom gas.

If into a Toricellian vacuum formed in a large bulb at the end of a long tube, there be admitted a quantity of glacial acetic acid, not sufficient to fill the space with saturated vapour, then at 20°, when the tension = 4mm., the vapour-density (reduced to 0° and to 0·76m. pressure) is equal to 3·74; and if the tension = 10mm. the vapour-density = 3·96 [so that, at this low temperature, acetic acid vapour is almost a monatomic gas]; at 30°, and 6mm. tension, the vapour-density is 3·60. (Bineau.)

Glacial acetic acid has a pungent sour taste and smell, and acts as an acrid poison. It does not redden litmus-paper *per se*, but very strongly on the addition of water. (Pelouze.)

Calculation, according to Gay-Lussac & Thénard, and Berzelius.

4 C	24	40·00
4 H	4	6·67
4 O	32	53·33
$C^4H^4O^4$	60	100·00

According to the radical-theory, *Acetyl* = Ac = C^4H^3 with 3O forms *Acetylic acid* or hypothetically anhydrous acetic acid = $C^4H^3O^3 = AcO^3$; and this, with 1 At. basic water, forms *Hydrated Acetylic acid* or *Glacial Acetic acid* = $HO,C^4H^3O^3 = HO,AcO^3$. According to this formula, the atomic weight of acetylic acid is $(24C + 3H + 27O) = 51$, and 100 pts. glacial acetic acid contain 85 pts. hypothetically anhydrous acetic acid and 15 pts. basic water.—¶ Kolbe (*Ann. Pharm.* 75, 211,) regards acetic acid as a copulated compound containing methyl and oxalic acid, $= HO,(C^2H^3),C^2O^3$. — According to Williamson and Gerhardt (VII, 19, 201) glacial acetic acid is $\left.\begin{matrix}C^2H^3O\\H\end{matrix}\right\}O$, or the hydrated oxide of a radical, C^2H^3O (called *Othyl* by Williamson, and *Acetyl* by Gerhardt), formed from ethyl, C^2H^5, by the substitution of 1 At. O for 2 At. H. The anhydrous acid (which Gmelin calls *hypothetically* anhydrous, but which has lately been obtained by Gerhardt), is according to the same view, $\left.\begin{matrix}C^2H^3O\\C^2H^3O\end{matrix}\right\}O$; vid. pp. 201. ¶

Decompositions. — 1. The vapour of acetic acid passed through a red-hot tube undergoes but very slight decomposition; but in presence of carbon or metals, it is completely resolved into carbonic acid, marsh-gas, empyreumatic oil, and acetone. — When the vapour of glacial acetic acid is passed through a red-hot glass tube, the greater part of the acid passes over undecomposed, but acquires a brownish colour and empyreumatic odour, and evolves but small quantities of carbonic acid and marsh-gas; if an iron tube be used, the glacial acetic acid is completely resolved into 1 vol. carbonic acid gas and 3 vol. marsh-gas, and the inner surface of the tube becomes coated with yellow ferric oxide. (Trommsdorff.) [The carbonic acid and marsh-gas should be produced in equal volumes:

$$C^4H^4O^4 = 2CO^2 + C^2H^4;$$

but since, by the oxidation of the iron, part of the carbonic acid is converted into carbonic oxide, the proportion of combustible gas actually obtained is greater.] — Concentrated acetic acid of sp. gr. 1·0635 (containing 54 p. c. of glacial acid) passed five times through a red-hot porcelain tube, gives off carbonic acid and carburetted hydrogen, and becomes empyreumatic, brownish, and much weaker; but if the tube be filled with charcoal, the acid, even at its first passage, is completely resolved into carbonic acid, carburetted hydrogen, and water. (Chenevix.) — Strong acetic acid passed in the state of vapour through a tube of porcelain or iron filled with charcoal and kept at a dull red heat, is completely resolved into a mixture of combustible gases, and a liquid consisting merely of water and pure acetone, which latter rises for the most part to the surface on saturating the water with chloride of calcium; if the tube be somewhat more strongly heated, no acetone is obtained but only combustible gases (Liebig & Pelouze, *Ann. Pharm.* 19, 296):

$$2C^4H^4O^4 = C^6H^6O^2 + 2HO + 2CO^2.$$

Spongy platinum in the tube decomposes the acetic acid vapour, even at a moderate heat; pumice-stone does not. At a higher temperature, however, decomposition is effected by pumice-stone as well as by platinum, but the gases then evolved are totally different from those which are produced under the influence of platinum at a lower temperature. (Reiset & Millon, *N. Ann. Chim. Phys.* 8, 290.) — ¶ According to Berthelot (*N. Ann. Chim. Phys.* 33, 295), acetic acid vapour passed through a red-hot porcelain tube filled with pumice-stone is but partially decomposed, the greater part remaining unaltered. The decomposition-products collected as completely as possible in a series of connected vessels cooled and partly filled with water, nitric acid, or potash, were found to consist of naphthalin, a small quantity of phenol, benzol (converted by the nitric acid into nitrobenzol), acetone, a peculiar yellowish white solid substance, and a brownish red solid having an odour of musk. The odour of the escaping gases resembled that of sea-fish, and was likewise empyreumatic; the gases contained carbonic acid. ¶

2. Glacial acetic acid heated in the air to its boiling point, and set on fire, *burns* with a very dull blue flame.

For the decomposition of acetic acid by electrolytic action, *vid.* VII, 247.

For the spontaneous decomposition of the acetic acid contained in crude vinegar, *vid. Acetic Fermentation.*

3. Dry chlorine gas, confined in a bottle together with glacial acetic acid, does not act upon it in the dark and but slowly in diffused daylight,

but quickly in sunshine, so that on hot days the reaction sometimes in the beginning amounts to an explosion, and on opening the bottle the resulting hydrochloric acid rushes out with force. If no explosion takes place, white fumes are formed which condense on the upper part of the vessel in the form of a heavy liquid;—also a large quantity of hydrochloric acid gas smelling of phosgene and producing turbidity in lime-water, an effect which may be attributed either to the phosgene or to carbonic acid;—*oxalic acid* and *terchloracetic acid*, C^4Cl^3H,O^4, crystallized on the sides of the vessel;—an uncrystallizable acid, produced in particular abundance when the glacial acetic acid is in excess [chloracetic acid ?]—sometimes also an oil resembling Dutch liquid, but different from that body and also from chloroform. This substance is most abundantly formed when the acetic acid is in excess, and the vessel is exposed to feeble daylight; it partly separates on mixing the whole liquid with carbonate of soda, and is partly obtained when the liquid thus neutralized is subjected to partial distillation, the oil then passing over first. (Dumas, *Ann. Chim. Phys.* 73, 75; also *Ann. Pharm.* 32, 106; also *J. pr. Chem.* 17, 202.)—If the dry chlorine acts only in diffused daylight, chloracetic acid, C^4ClH^3,O^4, is produced (Leblanc, *N. Ann. Chim. Phys.* 10, 212.)

Concentrated acetic acid, through which chlorine gas has been passed for some hours, gives off when distilled a strongly smelling vapour, which attacks the eyes painfully; besides this, nothing passes over but chlorine and acetic acid; no succinic acid is formed. (Liebig, *Pogg.* 15, 570.)—Glacial acetic acid exposed to sunshine in a bottle filled with chlorine, produces a white fume which condenses in the form of an oil and in crystals; it likewise gives off a small quantity of hydrochloric acid gas and a large quantity of phosgene, and the residual liquid contains hydrochloric acid, acetic acid, and an oily substance. (Matteucci, *Bibl. univ.* 50, 134.)—Chloride of lime distilled with an equal weight of acetate of lime yields a large quantity of chloroform (Bonnet, VII, 343); so likewise does chloride of lime or hypochlorite of soda with acetate of soda. (Böttger, Resch. *ibid.*)—Respecting the reaction of wine-vinegar with chloride of lime, *vid.* Liebig, *Repert.* 13, 280).

4. *Bromine* dissolves very readily in acetic acid, and decomposes it slowly, with formation of hydrobromic acid. (Balard.) It acts much less strongly than chlorine, and forms a liquid containing bromine; sometimes also small crystals are formed. (Matteucci.)—Bromine dissolves abundantly and without decomposition in an aqueous solution of acetate of potash, soda, or lime. The brown solution loses its colour when evaporated either at ordinary temperatures or with the aid of heat, giving off bromine, exhaling the odour of the alkaline hypobromites, and leaving an undecomposed acetate. (Cahours, *N. Ann. Pharm.* 19, 485.)—*Iodine* does not act upon acetic acid even in sunshine.

5. Acetic acid boiled with aqueous *Iodic* or *Periodic* acid yields carbonic acid, water and iodine; on boiling it with diperiodate of soda, iodate and formiate of soda are produced (Benckiser, *Ann. Pharm.* 17, 258):

$$C^4H^4O^4 + 2(2NaO,IO^7) = 2(NaO,IO^5) + 2C^2HNaO^4 + 2HO.$$

Free iodic acid exerts no decomposing action. (Millon.) *Nitric* acid is likewise without action on acetic acid of sp. gr. 1·007. (Darracq.)

6. A mixture of glacial acetic acid and *Oil of Vitriol* blackens when heated, giving off carbonic and sulphurous acid gases and hydrated acetic

acid. (Berzelius, *Lehrb.*) — Glacial acetic acid distils off undecomposed from its mixture with oil of vitriol [?], and even when mixed with peroxide of manganese and sulphuric acid, it is not decomposed, nor does it yield formic acid. (Matteucci, *Ann. Chim. Phys.* 52, 134.)

7. Acetic acid slowly reduces teroxide of gold, without evolution of carbonic acid. (Pelletier.)

Combinations. With *Water.* *Aqueous Acetic acid.* When it contains much acid it is called *Concentrated Vinegar;* when more dilute, *Distilled Vinegar.* — Preparation (p. 284). — Glacial acetic acid absorbs water from the air. It mixes with water without much evolution of heat (Gehlen), but the act of mixture is accompanied by great condensation. (Mollerat.) Glacial acetic acid precipitates many salts completely from their aqueous solution, by abstracting the water. In this manner are precipitated phosphate of magnesia, mono-arseniate of lime, and the sulphates of magnesia, cerous oxide, glucina, yttria, alumina, uranic oxide, manganous oxide, zinc-oxide, ferrous oxide, cobalt-oxide and nickel-oxide. But the sulphates of potash and soda, and the chlorides of potassium and sodium are not precipitated; neither are the majority of nitrates; but the nitrates of zinc, cobalt and nickel, are precipitated on the addition of sulphate of potash. (Persoz, *Ann. Chim. Phys.* 63, 443.) — Glacial acetic acid heated with sulphate of soda deprives it of its water of crystallization, and separates it in the anhydrous state; on the other hand, anhydrous sulphate of soda dissolved in hot concentrated acetic acid containing 5 per cent. of water, crystallizes on cooling in combination with water of crystallization. (Sébille-Auger.)

Percentage of Glacial Acetic acid in the Aqueous acid.

According to Mohr (*Ann. Pharm.* 31, 284.) [At what temperature?]

Perc.	Sp. gr.	Perc.	Sp. gr.	Perc.	Sp. gr.	Perc.	Sp. gr.	Perc.	Sp. gr.
100	1·0635	80	1·0735	60	1·067	40	1·051	20	1 027
99	1·0655	79	1·0735	59	1·066	39	1·050	19	1·026
98	1·0670	78	1·0732	58	1·066	38	1·049	18	1·025
97	1·0680	77	1·0732	57	1 065	37	1·048	17	1·024
96	1·0690	76	1·0730	56	1·064	36	1·947	16	1·023
95	1·0700	75	1·0720	55	1·064	35	1·046	15	1·022
94	1·0706	74	1·0720	54	1·063	34	1·045	14	1·020
93	1·0708	73	1·0720	53	1·063	33	1·044	13	1·018
92	1·0716	72	1·0710	52	1·062	32	1·042	12	1·017
91	1·0721	71	1·0710	51	1 061	31	1·041	11	1·016
90	1·0730	70	1·0700	50	1·060	30	1·040	10	1·015
89	1·0730	69	1·0700	49	1·059	29	1·039	9	1·013
88	1·0730	68	1·0700	48	1·058	28	1·038	8	1·012
87	1·0730	67	1·0690	47	1·056	27	1·036	7	1·010
86	1·0730	66	1·0690	46	1·055	26	1·035	6	1·008
85	1·0730	65	1·0680	45	1·055	25	1·034	5	1·007
84	1·0730	64	1·0680	44	1·054	24	1·033	4	1·005
83	1·0730	63	1·0680	43	1·053	23	1·032	3	1·004
82	1·0730	62	1·0670	42	1·052	22	1·031	2	1·002
81	1·0732	61	1·0670	41	1·051	21	1·029	1	1·001

According to this table, an acid of 79 — 80 p. c. has the greatest specific gravity; but between 90 and 76 there is but very little variation.

Mollerat and Ad. van Toorn (*J. pr. Chem.* 6, 171) have also given tables of the specific gravities of acetic acid of different degrees of concentration.

According to Mollerat, 100 pts. of glacial acetic acid of sp. gr. 1·063 form with 32·25 pts. of water, the densest mixture, the sp. gr. of which is 1·0791, and with 112·2 pts. water, a mixture whose density is the same as that of glacial acetic acid, viz. 1·063; and on further addition of water, the density is still further diminished. — When glacial acetic acid, not quite anhydrous is left to congeal at — 4°, and the mother-liquor drained off at that temperature, the liquid so obtained is $HO,C^4H^4O^4$, and has a density of 1·075. (Berzelius, *Lehrb.*)

Strong aqueous acetic acid does not solidify at — 30°; from the more dilute acid the water crystallizes out on cooling. — The more concentrated acid exposed in the piezometer to a pressure of 1100 atmospheres, crystallizes, leaving only $\frac{1}{16}$ in the liquid state, and this residual liquid when separated from the crystallized acid [glacial acetic acid?] exhibits but a slight acid reaction. (Perkins, *Pogg.* 9, 554.) — The aqueous acid boils above 100°, and exhibits the taste and odour of acetic acid, but in a less degree in proportion to its dilution.

Strong vinegar of 9° or 10° Bm. dissolves, at a boiling heat, a tolerably large quantity of *phosphorus*, some of which also is found in the distillate. The solution deposits part of the phosphorus as it cools, becomes very turbid on being mixed with water, smells of phosphorus and of acetic acid, and fumes in the air. (Bendet, *J. Pharm.* 1, 169.)

Strong vinegar dissolves *Boracic* acid, and mixes with aqueous *Phosphoric*, *Sulphuric*, *Hydrochloric*, and *Nitric* acid.

Glacial acetic acid unites with nitrous acid and nitric oxide, producing compounds, the former of which exhibits the blue colour of nitrous acid. On distilling acetate of soda with sulphate of nitric oxide, a blue distillate is obtained. — Crystals of glacial acetic acid placed in a tube through which nitric oxide gas is passed, assume a fine blue colour, and deliquesce to a blue liquid, solidifying in the cold to crystalline laminæ, which, when immersed in water, give off gas-bubbles, and move backwards and forwards by jumps. On passing nitric oxide gas through melted glacial acetic acid, the latter acquires a yellow colour, continually deepening in intensity and resembling that of nitric acid; it then becomes colourless, then greenish, afterwards sky-blue, and lastly almost colourless again. This mixture no longer crystallizes at + 6°, because it has absorbed too much moisture from the gas. It gives off scarcely any nitric oxide gas when boiled, but a large quantity on being mixed with water; it turns brown when mixed with oil of vitriol. — If the crystals of glacial acetic acid over which the nitrous gas is passed are placed in an open boiler, they quickly deliquesce to a dark blue liquid which gives off dark red vapours when heated; and these, when passed into a cold receiver, condense to a blue liquid containing nitrous and acetic acid, and not solidifying at — 12°. The colourless residue gives off dark red vapours every time that it is heated; but even after long-continued boiling, it still retains nitric oxide. (Reinsch. *J. p. Chem.* 28, 395.)

Acetates. — Many carbonates are not decomposed by acetic acid in its most concentrated state, either alone or on the addition of absolute alcohol; but decomposition takes place immediately on the addition of water. — Acetic acid in its most concentrated state does not act on native carbonate of baryta till a certain quantity of water has been added to it. (Berthollet, *Stat. Chim.* 2, 50.) — Glacial acetic acid and its mixture with absolute alcohol do not decompose carbonate of lime. (Zeise, *Dissertat.* 1817;) Unverdorben, *Pogg.* 11, 551; Pelouze, *Ann. Chim.*

Phys. 50, 314; also *Pogg.* 26, 343; also *Ann. Pharm.* 5, 268.) — The decomposition of carbonate of lime by glacial acetic acid does not take place either on continued boiling, or in the Torricellian vacuum, or under a pressure of 10 atmospheres. Lime obtained by igniting marble disappears immediately in glacial acetic acid, dissolving as acetate of lime in the excess of acid. The dry carbonates of potash, soda, zinc, and lead, are decomposed pretty quickly by glacial acetic acid; the carbonates of baryta, strontia, and magnesia, very slowly; but as soon as water is added, the decomposition becomes violent. A mixture of 1 vol. glacial acetic acid and several volumes of absolute alcohol does not decompose either of these salts, the decomposition only taking place on the addition of considerable quantities of water. If then such an alcoholic mixture be passed up to a concentrated solution of carbonate of potash standing over mercury, the carbonate of potash is precipitated from its aqueous solution by the alcohol, without decomposition, and in the form of a granular powder. (Pelouze.)

The alkaline monoacetates, and the monoacetates of magnesia, zinc, and lead, exhibit a slight alkaline reaction. (Morveau.) Most acetates when subjected to dry distillation yield acetone, an empyreumatic oil (dumasin = mesitic ether = $C^{12}H^{10}O^2$), and carbonic acid. The acetates of the fixed alkalis, when carefully distilled, are almost wholly resolved into acetone and alkaline carbonate, but if rapidly distilled, they also yield empyreumatic oil:

$$2C^4H^3BaO^4 = 2(BaO,CO^2) + C^6H^6O^2.$$

This simple decomposition succeeds best on carefully heating dry acetate of baryta; the acetone which passes over does not redden litmus, and the residual carbonate of baryta contains only a trace of charcoal. If, however, the heat be too suddenly applied, a certain quantity of empyreumatic oil goes over with the acetone, and charcoal remains in the residue, part of the evolved acetone being in fact decomposed by the strong heat into this oil and charcoal. (Liebig, *Pogg.* 24, 291.) — The earths and heavy metallic oxides, having less affinity for acetic acid, allow a larger or smaller quantity of it to pass over undecomposed, another portion being resolved into acetone and carbonic acid, and if the heat be strong, also into empyreumatic oil and charcoal; moreover, several heavy metallic oxides are at the same time reduced to the metallic state, with formation of carbonic acid and water. The residue therefore consists either of metal or oxide, mixed with charcoal. — The formation of acetone by dry distillation is characteristic of the acetates (and of the citrates), inasmuch as no other salts yield that product. — For Chenevix' tables on the behaviour of the individual acetates when subjected to dry distillation; vid. (*Gilb.* 32, 179.) — All acetates mixed with large quantities of the hydrate of a fixed alkali, and heated to a temperature considerably below redness, are completely resolved into marsh-gas and alkaline carbonate. (Persoz, Dumas, *Ann. Chim. Phys.* 73, 92; also *J. pr. Chem.* 21, 260):

$$C^4H^3KO^4 + HO,KO = 2(KO,CO^2 + C^2H^4.$$

Such a decomposition takes place when 1 pt. of crystallized acetate of soda is heated with 4 pts. of baryta or with 1 pt. hydrate of potash and 3 pts of lime. (Dumas.) — Acetate of potash (and probably also other fixed alkaline acetates) mixed with arsenious acid, and slowly heated to redness, give off alkarsin, together with other products. (Cadet, Bunsen.)

Assuming that the essential products of this decomposition are merely alkarsin and carbonic acid, the equation will be:

$$2C^4H^3KO^4 + AsO^3 = \underbrace{C^4H^6AsO}_{\text{Alkarsin.}} + 2(KO,CO^2) + 2CO^2.$$

[For a more exact account of this decomposition, vid. *Alkarsin.*] — Hence to ascertain whether a given acid is acetic acid, saturate it with potash, mix with pulverized arsenious acid, evaporate to dryness, and heat the residue in a test-tube. If acetic acid be present, alkarsin will be formed, and may be recognized by its remarkable odour. (Bunsen.) The dilute aqueous solutions of acetates, especially those of the alkalis and earths, decompose by long keeping, with formation of carbonates and fungi. — ¶. A neutral solution of an alkaline acetate left to stand in contact with putrefying animal mucus, putrid liver, solution of emulsin, or beer-yeast, is converted in a few weeks into carbonate, (Buchner, *Ann. Pharm.* 78, 203; *Jahresber.* 1851, 375.) ¶. — Acetates treated with sulphuric, phosphoric, hydrochloric, or nitric acid, give out the odour of acetic acid. — Acetates distilled with dilute sulphuric acid yield a distillate, which, when agitated with oxide of lead at ordinary temperatures, acquires an alkaline reaction. (Liebig.) — All neutral acetates dissolve in water, and most of them readily. Solutions of ferric salts diluted till they exhibit a pale yellow tint, are coloured reddish yellow by solutions of the neutral acetates; more concentrated ferric solutions acquire a red-brown colour, which however changes again to the original yellow on the addition of a few drops of hydrochloric acid. On boiling the mixture of an alkaline acetate and a ferric or chromic salt, the iron or chromium is thrown down as a basic salt of the sesquioxide. — The aqueous solutions of other acetates added to mercurous nitrate or silver-nitrate throw down delicate white shining scales of mercurous acetate or silver-acetate.

ACETATE OF AMMONIA. — *a. Neutral.* — In the state of aqueous solution: *Spiritus Mindereri.* — To obtain the anhydrous salt, glacial acetic acid or the acid salt heated till it melts is saturated with dry ammoniacal gas. (Liebig, *Chim. org.*) — Strong vinegar and strong ammonia produce great heat when mixed. (Geiseler, *N. Br. Arch.* 11, 240.) — This salt is difficult to obtain in the crystalline state, because, when its aqueous solution is evaporated, it gives off ammonia and is converted into the acid salt. Thomson, (*Ann. Phil.* 14, 145), by dissolving carbonate of ammonia in strong acetic acid, and evaporating the filtrate in vacuo over oil of vitriol, obtained thin prisms which reddened litmus but feebly. The aqueous solution of this salt obtained by saturating aqueous acetic acid with carbonate of ammonia or pure ammonia, is transparent and colourless; has a peculiar odour and a cooling pungent taste; becomes alkaline when kept in the dilute state, the acetic acid being decomposed and carbonate of ammonia formed together with flocculent matter; and is converted by heat into a solution of *b.* — Chlorine decomposes part of the ammonia, with formation of sal-ammoniac. (L. A. Buckner, *Repert.* 64, 13.) When the aqueous solution is left to evaporate in sunshine in a shallow dish placed under a bell-jar, it becomes syrupy without turning sour; and if afterwards mixed with a concentrated solution of chloride of calcium, it becomes heated, and forms so thick a mixture, from separation of acetate of lime, that it does not run out when the vessel is inverted. (Brendecke, *Repert.* 55, 321.) — [Respecting the preparation of Sp. Mindereri, *vid.* especially Mohr. (*Ann. Pharm.* 31, 277.)] — The salt is soluble in alcohol.

¶ From the gummy liquid formed on agitating a solution of acetate of ammonia with recently precipitated and still moist mercuric oxide. Hirzel (*Zeitchr. Pharm.* 1851, 2; *Jahresber.* 1851, 437) obtained crystals which, when recrystallized by spontaneous evaporation of their solution in cold water, yielded transparent, colourless, rectangular tables, having the composition $C^4H^3(NH^4)O^4,HgO$. They were very soluble in water, almost insoluble in alcohol, smelt of acetic acid, and decomposed gradually on exposure to the air.

b. Acid. — 1. A dry mixture of sal-ammoniac with an equal weight of acetate of potash or lime gives off ammonia when heated, and yields the acid salt in the form of a crystalline sublimate. When the saturated solution of this mixture is kept in a well-closed bottle, long needles separate from it. (Berzelius, *Lehrb.* — 2. The aqueous solution of the neutral salt gives off ammonia when evaporated, turns acid, and finally solidifies in a radiated mass on cooling. The crystals fuse at 76°, and sublime undecomposed at 121°. They redden litmus and deliquesce in the air. (Lassone, *Crell. J.* 5, 71.) This salt probably contains 2 At. acid, corresponding to the potash and soda-salt.

ACETATE OF POTASH. *a. Neutral.* — *Foliated Earth of Tartar, Geblätterte Weinsteinerde, Blättererde, wiederdergestellter Weinstein, Terra foliata Tartari, Arcanum Tartari, Tartarus regeneratus.*

Preparation. 1. By neutralizing carbonate of potash with acetic acid evolved from an acetate by sulphuric acid, and evaporating. — If instead of acetic acid thus prepared, we use distilled vinegar containing more or less matter (extractive or gummy?) which is browned by potash, the mixture must be evaporated with continual addition of acetic acid, so that the potash may never be in excess from evaporation of the acetic acid, as that would cause browning; — or the mixture may be evaporated without this precaution; the concentrated liquid decolorized by boiling with charcoal-powder; and the filtrate evaporated to dryness, after being neutralized, if necessary, with strong acetic acid; — or the mixture may be immediately evaporated to dryness; the brown saline mass fused, either alone or with the addition of one-tenth of its weight of charcoal-powder; the fused mass dissolved; the liquid filtered; any carbonate of potash that may have been reproduced, neutralized with strong acetic acid; and the solution evaporated to dryness. If the acetic acid has been neutralized, not with carbonate of potash prepared from the tartrate, but with pearl-ash, the resulting acetate contains a considerable quantity of chloride of potassium and sometimes also sulphate of potash.

2. By precipitating an aqueous solution of neutral acetate of lead with carbonate or sulphate of potash in equivalent proportion, separating the last traces of lead by sulphuretted hydrogen, and evaporating the filtrate to dryness. — *Carbonate of potash*, especially that which is prepared from cream of tartar, is preferable to the sulphate for this purpose. It must be added, cold or gently warmed, to the lead solution, till the mixture slightly reddens turmeric paper; the liquid filtered after several hours; sulphuretted hydrogen passed through it for ten minutes; the liquid, which thereby becomes brownish, heated till black flakes separate from it, then acidulated with somewhat concentrated vinegar, digested for a while, and lastly filtered and evaporated. (Wackenroder, *N. Br. Arch.* 15, 171.)

When acetate of lead is precipitated by *sulphate of potash*, the sulphate of lead carries down with it a quantity of sulphate of potash, greater as the mixture is colder and more concentrated; and if equivalent quantities are used (190 pts. acetate of lead to 87·2 sulphate of potash), a large quantity of undecomposed sugar of lead remains in the liquid. As this inconvenience is to be avoided only by the use of large quantities of water, and by several hours' boiling, it is better to use an excess of sulphate of potash. To a boiling solution of 190 pts. acetate of lead in a fourfold quantity of water, add 150 pts. sulphate of potash dissolved in a sixfold quantity of water; boil for a quarter of an hour, decant, filter, wash well with boiling water, evaporate the filtrate to $\frac{1}{2}$ of its bulk; remove the remaining lead by sulphuretted hydrogen; concentrate the filtrate so far that the sulphate of potash may crystallize out on cooling; and evaporate to dryness the liquid decanted therefrom. (Trommsdorff, *Taschenb.* 1825, 1.) — The same process had been previously recommended by Pontet. (*J. Pharm.* 1, 203.)

The dry salt melts below a red heat, to an oily liquid, which on cooling solidifies in a white, opaque, crystalline mass. If it be melted in a spoon and then left to cool, long crystals grow out of the mass, their forms being particularly beautiful if the salt has not been completely melted. (Marx, *J. pr. Chem.* 24, 142.) — The aqueous solution, if gradually evaporated and stirred all the while, becomes covered with a crust of anhydrous salt, which renews itself as fast as it is skimmed off, till the whole liquid is converted into a dry pulverulent mass. A solution highly concentrated by evaporation, and then left to stand for some time in the cold, yields large transparent prisms of the hydrated salt. The salt has a warm and pungent saline taste.

	Dehydrated.		Wenzel.	Richter.	Higgins.
KO	47·2	48·07	50·15	51·4	61·5
$C^4H^3O^4$	51·0	51·93	49·85	48·6	38·5
$C^4H^3KO^4$	98·2	100·00	100·00	100·0	100·0

Acetate of potash subjected to dry distillation, yields acetic acid, acetone, empyreumatic oil, water, carbonic acid, a combustible gas, and carbonate of potash mixed with a small quantity of charcoal. (Trommsdorff.) According to Fourcroy, the residue is pyrophoric, but according to Proust it is not. — [For the formation of alkarsin by heating acetate of potash with arsenious acid, *vid.* p. 296.] — When acetate of potash is heated with aqueous hypochlorous acid, acetic acid, chlorine, and a small quantity of oxygen are evolved, and chlorate of potash formed. (Balard.) The salt dissolved in a large quantity of water, changes after some time into carbonate, with formation of fungi. — Triturated with iodine it assumes an indigo colour, which changes to brown on the addition of water. (Grundner, Vogel, *N. Br. Arch.* 16, 153.) — The salt deliquesces very easily in the air; dissolves at 2° in 0·531, at 13·9° in 0·437, at 28·5° in 0·321, and at 62° in 0·203 pts. of water. (Osann.) A solution saturated at the boiling heat contains only 0·125 pt. water to 1 pt. salt, and boils at 169°. (Berzelius, *Lehrb.*) — It dissolves in 3 pts. of cold and 2 pts. of hot absolute alcohol. (Destouches.) Carbonic acid gas passed through a solution of the salt in alcohol of 97 p. c., or in absolute alcohol, throws down a considerable quantity of carbonate of potash, and produces a large quantity of acetic ether. (Döbereiner, *Ann. Pharm.* 14, 209.)

b. Biacetate. — When strong acetic acid in excess is evaporated in contact with neutral acetate of potash, the biacetate crystallizes from the residue in nacreous, very flexible, and easily cleft needles and laminæ, which may be dried between filtering paper; or if the mixture be slowly cooled, in long flat prisms belonging to the right prismatic system. The salt, after being dehydrated in dry air, loses only ·002 or ·003 of its weight by exposure to a heat of 120° in vacuo. — It melts at about 148°, giving off a mere trace of acid, the separation of which is probably due to moisture in the air, and solidifies again in the crystalline form on cooling. At 200° it boils, gives off glacial acetic acid, the heat rising to 300°, and leaves a residue of monoacetate of potash, which at a still higher temperature likewise melts and is decomposed. — When the salt is exposed to a current of aqueous vapour, dilute acetic acid goes off, and monoacetate of potash remains behind. — [An example of reciprocal affinity, according to the quantity of water present.] — The acid salt deliquesces in the air, but not so quickly as the neutral salt. It dissolves sparingly in cold, abundantly in hot alcohol, so that the hot solution solidifies on cooling; on boiling the solution, alcohol containing acetic acid is evolved. (Melsens, *Compt. rend.* 19, 611; also *J. pr. Chem.* 33, 449.)

	Dried at 120° *in vacuo.*		Melsens.
8 C	48·0	30·34	29·75
7 H	7·0	4·42	4·35
K	39·2	24·78	25·00
8 O	64·0	40·46	40·90
$C^4H^3KO^4,C^4H^4O^4$	158·2	100·00	100·00

On adding acetic acid to a concentrated solution of fluoride of potassium in sufficient quantity to neutralize it, and evaporating carefully to dryness to drive off any excess of acetic acid (if too much heat were applied, all the acetic acid would go off), there remains a compound which exhibits a neutral reaction when dissolved in a small quantity of water, but becomes acid on dilution, the acetic acid then uniting again with the water. (Berzelius, *Pogg.* 1, 12.)

ACETATE OF SODA.— *a. Neutral.* — *Krystallisirte Blättererde, Terra foliata Tartari crystallisabilis.* — Obtained by neutralizing distilled or concentrated vinegar with carbonate of soda and evaporating, — or by precipitating acetate of lead with excess of carbonate of soda, evaporating the filtrate after neutralizing with acetic acid and treating with sulphuretted hydrogen, —and leaving the solution to crystallize in an open dish. The crystals, after being freed from the mother-liquid, are dehydrated by heating and stirring them about all the time. — The dry salt is white and fusible, sustains, according to Thomson, a heat of 288° without decomposition, and does not begin to char till it is heated to 315°. — If the dry salt be fused and left to cool in a large platinum spoon, it separates suddenly, while still fluid, from the sides of the spoon, becomes crystalline in the middle, and covers itself with a crust, through which a number of nacreous crystals shoot out from the interior, ½ of an inch long and broad, and having a great number of sharply defined faces to which cleavage-planes correspond. By exposure to the air these crystals become dull and pulverulent. (Marx, *Schw.* 52, 360.) — The experiment does not always succeed, the salt often solidifying quietly in a radiated crystalline mass. A portion of the salt which has once exhibited this phenomenon, does not exhibit it again, or at least but imperfectly, if melted a second time,

unless the crust which forms on the surface be pierced. The peculiar property is not restored by solution in water and evaporation, but it is restored by solution in acetic acid and evaporation; hence its disappearance seems to arise from loss of acetic acid at the second melting. (Schweigger-Seiddel, *Schw.* 54, 27.) — The salt yields by dry distillation a mixture of 1 vol. carbonic acid gas and 1 vol. marsh-gas, a brown liquid consisting of water, acetic acid, empyreumatic oil and acetone, and leaves carbonate of soda mixed with charcoal. (Trommsdorff.) Acetate of soda in crystallizing from water exhibits very strikingly the anomaly described in vol. I, pp. 9—12. The hydrated crystals are transparent prisms belonging to the oblique prismatic system. *Fig.* 113; cleavage parallel to *i*, *u* and *u'*; $i:u$ or $u'=104° 25'$; $i:a$ about $=136°$; $i:f=103° 35'$; $u:u'=84° 30'$; $u:m=137° 45'$; $u:t=132° 15'$; $u:k=156° 54'$; $u:h=135° 30'$. (Brooke, *Ann. Phil.* 22, 39.) The crystals have a saline, bitter taste, effloresce slightly in the air, completely at a moderate heat, and melt below 100°. — The salt yields with iodine a black-violet mixture, which becomes yellowish brown when brought in contact with water. (Vogel.) It dissolves in 2·86 pts. cold water (Bergman); in 3·9 pts. at 6°, in 2·4 pts. at 37°, and in 1·7 pt. at 48°. (Osann.) A solution saturated at a boiling heat contains 0·48 pt. water to 1 pt. salt, and boils at 124·4°. (Berzelius, *Lehrb.*) — A solution of 1 pt. of the crystallized salt in 2 pts. water has a density of 1·100, and boils at 103·6°; in 5 pts. water, 1·060 and 101·7°; in 10 pts. water, 1·030 and 100·8°. (Brandes, *Br. Arch.* 22, 147.) — The salt dissolves in 2·1 pts. of boiling highly rectified spirit (Wenzel), and is precipitated from the cold solution by ether in the form of a crystalline powder. (Döbereiner.)

Dry.			Berzelius.	Gehlen.	Wenzel.	Richter.
NaO	31·2	37·96	38·311	37·93	39·67	44·6
$C^4H^3O^3$	51·0	62·04	61·689	62·07	60·33	55·4
$C^4H^3NaO^4$	82·2	100·00	100·000	100·00	100·00	100·0

Crystallized.			Berzelius.
NaO	31·2	22·91	22·94
$C^4H^3O^3$	51·0	37·44	36·95
6 Aq	54·0	39·65	40·11
$C^4H^3NaO^4 + 6Aq$	136·2	100·00	100·00

From a more dilute solution, Anthon (*Repert.* 76, 346) once in summer obtained crystals containing 49·5 p. c. (9 At.) water.

b. Biacetate. — Mentioned by Graham. (*Lehrb.*)

Sulphacetate of Soda? — When acetate of lime is decomposed by sulphate of soda in excess, or even in less than the equivalent quantity, part of the sulphate of soda remains in the liquid undecomposed, and the crystals which separate on evaporating the filtrate contain 6·2 per cent. of sulphate of soda united with the acetate. (Mill, *Ann. Phil.* 26, 113.)

Acetate of Lithia. — The salt dehydrated by fusion is white and opaque. At an incipient red heat it fuses to an oil, which froths up at a higher temperature, emitting the odour of empyreumatic oil and acetone, and when heated in the blowpipe flame, suddenly burns away with a beautiful violet-red flame, leaving a mixture of charcoal and carbonate of lithia. — From the aqueous solution, it crystallizes in hydrated, right

rhombic prisms an inch long, and often with their acute lateral edges truncated. It turns reddened litmus blue, and has a mild taste, sweetish at first, but afterwards agreeably saline. — The crystals do not effloresce in dry air; they fuse partially at 49° and completely at 70°, forming a viscid liquid, which at 25° gives off water, becomes more viscid, and on cooling solidifies to a transparent mass. It also solidifies when more strongly heated, swelling up at the same time. — It does not deliquesce in moist air. 1 pt. of the salt dissolves at 15° in 0·2833 pt. (therefore less than one-third) of water, forming a solution which solidifies completely at +4°. At 14°, it dissolves in 4·64 pts. alcohol of sp. gr. 0·81 and sparingly also in ether. (Pleischl, *Zeitschr. Phys. v. W.* 4, 108.)

Arfwedson & Turner (*Ed. J. Sc.* 3, 467) obtained the salt merely in the form of a gummy mass, which yielded a gummy solution with a small quantity of water.

Fused.			*Crystallized.*			Pleischl.
LO	14·4	22·02	LO	14·4	14·20	13·91
$C^4H^3O^3$	51·0	77·98	$C^4H^3O^3$	51·0	50·30	49·31
			4 Aq	36·0	35·50	36·78
$C^4H^3LO^4$	65·4	100·00	+4Aq	101·4	100·00	100·00

Acetate of Baryta. — Obtained by decomposing carbonate of baryta or sulphide of barium with strong acetic acid, then filtering, and evaporating to the crystallizing point. The salt obtained by precipitating sulphide of barium with acetate of lead has an unpleasant odour. (Funcke, *Br. Arch.* 4, 268.)

The dry salt obtained by heating the crystals to 100° is a white powder. When subjected to dry distillation, it is almost wholly resolved into acetone and carbonate of baryta (Chenevix, Liebig); and when heated with potassium or sodium, it is resolved without appearance of fire, into alkali and charcoal. (Gay-Lussac & Thénard.)

The concentrated aqueous solution of the salt left to evaporate spontaneously in summer, yields flat, four-sided, bevelled prisms containing 1 At. water. (Bucholz, *A. Tr.* 1, 2, 77; Mitscherlich.) — By cooling a less saturated solution to 0°, it is easy to obtain crystals with 3 At. water, which are isomorphous with those of neutral acetate of lead. (Mitscherlich.) They are large, transparent, shining prisms, belonging to the oblique prismatic system. *Fig.* 90°, without the *l*-face; cleavage distinct parallel to *i*, less distinct parallel to *t*, indistinct in a direction perpendicular to *t* and *i*; $u:u' = 126° 8'$ (126° 52′ according to Bernhardi); $u:t = 116° 56'$; $i:t = 113° 12'$; $i:f = 100° 30'$; $t:f$ *backwards* $= 146° 18'$ (Brooke, *Ann. Phil.* 23, 365); *comp.* Bernhardi (*Schw.* 4, 35), who found several additional faces. — The crystals effloresce in the air but retain their form. (Gehlen.) They have a pungent odour and slight alkaline reaction. They dissolve in 1·2 pts. of cold, and 1·1 of boiling water, and in 100 pts. of cold, and 67 of boiling hydrated alcohol (Bucholz), but are insoluble in absolute alcohol (Schlieper).

Dried at 100°.			Richter.	Bucholz.	Gay-Lussac & Thénard.
BaO	76·6	60·03	59·4	60·56	56·83
$C^4H^3O^3$	51·0	39·97	40·6	39·44	43·17
$C^4H^3BaO^4$	127·6	100·00	100·0	100·00	100·00

Crystals with 1 *At. Water.*

BaO	76·6	56·08	56·70
$C^4H^3O^3$	51·0	37·33	36·93
Aq	9·0	6·59	6·37
$C^4H^3BaO^4 + Aq$	136·6	100·00	100·00

Crystals with 3 *At. Water.*			Mitscherlich.
BaO	76·6	49·55	
$C^4H^3O^3$	51·0	32·99	
3 Aq	27·0	17·46	17·5
+3Aq	154·6	100·00	

ACETATE OF STRONTIA. — Prepared like the baryta-salt. Crystallizes from the aqueous solution at 15° in combination with 4·23 p. c. ($\frac{1}{2}$ At), and at a lower temperature with 26 p. c. (4 At.) water of crystallization. (Mitscherlich.) The latter crystals are transparent prisms belonging to the oblique prismatic system, which effloresce very readily. *Fig.* 90. Cleavage parallel to t somewhat more distinct than in other directions. $u:u' = 124° 54'$; $u:t = 107° 33'$; $t:i = 153° 12'$; $t:l = 122° 58'$; $t:f$ backwards $= 129° 20'$. (Brooke, *Ann. Phil.* 23, 288.) — Yields a large quantity of acetone by dry distillation. (Chenevix.) Tastes sharp and dissolves easily in water. (Vauquelin.) Less soluble in alcohol.

ACETATE OF LIME. — Formed by dissolving carbonate of lime in aqueous acetic acid and evaporating. Crystallizes in combination with water in needles and prisms, which effloresce partially in the air at ordinary temperatures, and completely at 100°, yielding a white powder. When subjected to dry distillation, it yields a large quantity of acetone. (Chenevix.) Not decomposed by carbonic acid gas, either in the dry state, or in the state of aqueous solution. (Pelouze.) — Soluble in water, less soluble in alcohol.

Dry.			Berzelius.	Higgins.	Richter.	Wenzel.
CaO	28	35·44	35·4	35·7	34·3	34·25
$C^4H^3O^3$	51	64·56	64·6	64·3	65·7	65·75
$C^4H^3CaO^4$	79	100·00	100·0	100·0	100·0	100·00

Acetate of Lime with Chloride of Calcium. — The aqueous solution of the two salts in equivalent proportions yields, by slow evaporation, large crystals, which are permanent in the air at ordinary temperature, effloresce when moderately heated, and at 100° give up all their water without change of form. (Fritzsche, *Pogg.* 28, 123.) The formation of this salt may serve perhaps to explain Schmidt's observation (*Mag. Pharm.* 13, 64), that chloride of calcium distilled with strong vinegar yields a distillate containing hydrochloric acid.

Crystallized.			Fritzche.
CaCl	55·4	24·69	25·00
$C^4H^3CaO^4$	79·0	35·20	35·55
10 Aq	90·0	40·11	39·45
$CaCl, C^4H^3CaO^4 + 10Aq$	224·4	100·00	100·00

Acetic acid dissolves a small quantity of *triphosphate* of lime, yielding by evaporation a translucent slightly deliquescent mass. (Wenzel.)

ACETATE OF MAGNESIA.—Crystallizes with difficulty, generally remaining, when its aqueous solution is evaporated, in the form of a colourless, very bitter, adhesive, slightly deliquescent gum, which yields acetic acid by distillation, and dissolves readily in water and alcohol. (Wenzel.) Ammonia added to the solution throws down only $\frac{1}{16}$ of the earth. (Pfaff.) The salt is distinguished from formiate of magnesia by its property of not crystallizing, and by its deliquescence. (Connell.)

	Dehydrated.			Wenzel.	Richter.
MgO	20	28·17	30·25	34	28·9
$C^4H^3O^3$	51	71·83	69·75	66	71·1
$C^4H^3MgO^4$	71	100·00	100·00	100	100·0

CEROUS ACETATE. — Delicate needles which are permanent in the air, melt and subsequently decompose in the fire, and dissolve very sparingly in alcohol. (Berzelius.)

ACETATE OF LANTHANUM. — Easily soluble in water. (Mosander.)

ACETATE OF YTTRIA. — Pale red, four-sided prisms, easily soluble in water. (Klaproth.) The neutral solution crystallizes readily by spontaneous evaporation; the acid solution leaves a thick syrup above the crystals. The rose-red crystals become colourless when recrystallized from water. They are rhombic and flat four-sided prisms acuminated with three faces. At 100°, they give off all their water and become opaque. They are permanent in the air, dissolve in 9 pts. of cold and a smaller quantity of warm water, and likewise in alcohol. (Berlin.)

	Crystallized.		Berlin.
YO	40	36·70	83·46
$C^4H^3O^3$	51	46·79	
2 Aq	18	16·51	16·54
$C^4H^3YO^4+2Aq$	109	100·00	100·00

ACETATE OF GLUCINA. — Not crystallizable, but forms a transparent, viscid gum, having a rough sweetish taste, and very soluble in water. (Vauquelin.)

ACETATE OF ALUMINA. — Obtained by dissolving the hydrate in the acid; by decomposing sulphate of alumina with acetate of lead; and in an impure state, by decomposing alum with acetate of lead. The liquid when evaporated yields a gummy mass, which reddens litmus, and has an astringent taste. Gives off its acid undecomposed at a temperature below redness. (Wenzel.) Deliquesces in the air. — The aqueous solution mixed with other salts, such as the sulphate of potash, soda, magnesia, and ammonia, chloride of sodium, alum, &c., becomes turbid when heated, and deposits alumina which re-dissolves on cooling. (Gay-Lussac, *Ann. Chim.* 74, 193; also *J. Phys.* 70, 139; also *Schw.* 5. 49; further, *Ann. Chim. Phys.* 6, 201; also *Schw.* 21, 96.) — It would appear from this that at high temperatures, acetic acid has a greater affinity for the foreign salts than for the alumina. — A solution of alum mixed with acetate of soda and gently heated, yields a precipitate of basic acetate of alumina, which does not redissolve even on the addition of acetic acid. When a solution of alum is precipitated by excess of acetate of lead, and

the lead removed from the filtrate by sulphuretted hydrogen, the liquid thus obtained (which besides acetate of alumina and acetate of potash likewise contains free acetic acid), becomes turbid between 90° and 100° and deposits a basic salt. (Ph. Büchner, *Ann. Pharm.* 53, 354.)—The liquid obtained by precipitating an aqueous solution of 6 parts acetate of lead with 5 pts. alum, and containing sulphate of potash from the alum as well as acetate of alumina, serves as a mordant, especially for dyeing cotton.

¶ The acetates of alumina have lately been more minutely investigated by Crum (*Chem. Soc. Qu. J.* VI, 217); the following are the principal results of the investigation.

1. The aluminous solution obtained by decomposing pure tersulphate of alumina with the neutral acetate of lead consists, apparently, of a mixture of biacetate of alumina with 1 At. free acetic acid. No true teracetate of alumina appears to exist.

2. When means are taken to evaporate the preceding aluminous solution at a low temperature with sufficient rapidity, a dry substance is obtained, which may be redissolved easily and entirely by water. This is the biacetate of alumina ($Al^2O^3,2C^4H^3O^3 + 4HO$), in which the alumina retains all its usual properties.

3. When the first aluminous solution, containing not less than 4 or 5 per cent. of alumina, is left for some days in the cold, a salt is deposited in the form of a white crust, which is an allotropic biacetate of alumina, containing 5HO water, insoluble in water. Heat effects a similar change in the aluminous solution more rapidly, and the new acetate precipitates as a granular powder containing 2HO. At the boiling temperature, the liquid is thus deprived, in about half an hour, of the whole of its alumina, which goes down with $\frac{2}{3}$ of the acetic acid, leaving $\frac{1}{3}$ in the liquid.

4. The soluble biacetate of alumina is decomposed by heat, and affords a new and remarkable product. When a dilute solution of that salt is exposed to heat for several days, the whole acetic acid appears to become free, and the alumina to pass into an allotropic condition, in which, although it remains in solution, it ceases to be capable of acting as a mordant or entering into any other definite combination. Indeed alumina in this altered state appears to be really soluble in pure water. The allotropic alumina retains 2 atoms of water, when dried at the heat of boiling water. Its solution is coagulated by the mineral and most of the vegetable acids, by the alkalies, by a great number of neutral salts, and by decoctions of dye-woods. This alumina is insoluble in the stronger acids, but soluble in acetic acid as well as in pure water, unless it has been previously coagulated by the means above mentioned, when it remains insoluble. It yields, however, to the continued action of boiling potash, which changes it into the ordinary terhydrate. Its coagulum with dye-woods has the colour of the infusion, but is translucent and entirely different from the dense opaque lakes which ordinary alumina forms with the same colouring matters.

5. The insoluble biacetate of alumina, when digested in a large quantity of water, is gradually changed into the soluble biacetate; of which a part, however, becomes decomposed during the process into acetic acid and the allotropic bihydrate of alumina.

6. The precipitate which is formed on the application of heat to a mixed solution of acetate of alumina and sulphate of potash, and which is soluble in cold acetic acid, is a bibasic sulphate of alumina. ¶

ACETATE OF THORINA. — Hydrate of thorina forms with dilute acetic acid a turbid, gummy, tenacious mass. The carbonate treated with strong acetic acid, effervesces and is reduced to a powder, but little of which dissolves in the excess of acid. If either of these masses be evaporated at a gentle heat nearly or quite to dryness, the acetate of thorina separates as an amorphous mass, scarcely soluble in water; when dry, it is heavy and milk-white. By this means thorina may be separated from other earths which remain dissolved; but on washing the residue with water, the liquid which passes through the filter is milky from suspended acetate of thorina, unless some sal-ammoniac be added to the water. — Acetate of potash added to a solution of neutral nitrate of thorina, produces no precipitate, even on the application of heat, probably in consequence of the formation of a double salt. (Berzelius, *Pogg.* 16, 413.)

ACETATE OF ZIRCONIA. — The solution of hydrate of zirconia in acetic acid yields, without crystallizing, a rough powder which does not deliquesce in the air, but dissolves readily in water and alcohol (Klaproth, Vauquelin); according to Berzelius, however, it is deliquescent.

ACETATE OF TITANIUM. — The solution yields on evaporation an amorphous jelly.

Tantalic oxide does not dissolve in acetic acid. (Hatchett.)

MOLYBDOUS ACETATE. — Formed by double decomposition. Dark grey precipitate, black after drying, slightly soluble in excess of acetic acid. (Berzelius, *Pogg.* 6, 379.)

MOLYBDIC ACETATE. — Acetate of potash forms with bichloride of molybdenum a rusty brown precipitate, which does not turn blue on exposure to the air, but dries up to a dark brown powder; while yet moist, it dissolves in boiling acetic acid, forming a yellow solution which gelatinizes on cooling, from separation of the neutral salt. (Berzelius, *Pogg.* 6, 349.)

ACETATE OF MOLYBDIC ACID. — The solution of molybdic acid in boiling acetic acid is turbid when the former is in excess; the filtrate yields by evaporation a colourless jelly, which when evaporated in the air, turns yellow, bursts asunder, and crumbles to a coarse yellow powder; it dissolves very sparingly in water, forming a yellow solution. (Berzelius, *Pogg.* 6, 384.)

VANADIC ACETATE. — Dilute acetic acid forms a pale blue solution with hydrated vanadic oxide; but the quantity dissolved is small, even at a boiling heat. Strong acetic acid dissolves somewhat more, forming a beautiful blue liquid which, when left to evaporate, turns green and deposits dark green microscopic cubes and short square prisms, which dissolve very slowly in water, forming a green solution. Concentrated solutions of acetate of potash and vanadic sulphate yield no precipitate when mixed. (Berzelius, *Pogg.* 22, 34.)

Vanadic acid does not dissolve even in the strongest acetic acid.

CHROMOUS ACETATE. — Dilute acetate of soda mixed in equivalent proportion with protochloride of chromium, CrCl, in a vessel from which the air is completely excluded, forms a violet-red liquid, quickly depositing

small, red, shining crystals, which dry up in vacuo and must be kept in bottles filled with carbonic acid or nitrogen. — On exposure to the air, they quickly change to a green powder, soluble in water, and if they are still somewhat moist, this oxidation rises to actual combustion. When burnt in the air, they deposit 40·2 per cent. of chromic oxide. They dissolve sparingly in cold water and alcohol, better in hot water, forming a red liquid which, when exposed to the air, soon assumes the violet colour of chromic salts. (Péligot, *N. Ann. Chim. Phys.* 13; also *J. pr. Chem.* 35, 34.)

			Péligot.
4 C	24	25·00	25·20
4 H	4	4·17	4·30
Cr	28	29·16	28·14
5 O	40	41·67	42·36
$C^4H^3CrO^4 + Aq$	96	100·00	100·00

Chromic Acetate. — The green solution of hydrated chromic oxide in acetic acid is precipitable by alkalis, and when evaporated at 25°, leaves a green saline crust permanent in the air and easily soluble in water. (Brandenburg, *Scher. Nord. Bl.* 1, 220.)

Uranous Acetate. — The solution of hydrated uranous oxide in aqueous acetic acid, evaporated in the air at a gentle heat, takes up oxygen and deposits the greater part of the uranium in the form of uranoso-uranic oxide. By spontaneous evaporation, a dark green mass is obtained, consisting of fine needles united in warty masses, but contaminated with a large quantity of uranic acetate. (Rammelsberg, *Pogg.* 58, 34.)

Uranic Acetate. — Obtained by heating uranic nitrate till it begins to evolve oxygen, dissolving the yellowish red mass, which still contains nitric acid, in warm concentrated acetic acid, and evaporating to the crystallizing point; the uranic nitrate then remains in the mother-liquid. (Wertheim.)

a. Crystals with 2 *At. Water.* These separate out on slightly cooling the solution, most distinctly from a very acid solution, and in yellow oblique rhombic prisms. At 275°, they give off 8·32 p. c. water and turn yellowish red. They dissolve in boiling water with separation of hydrated uranic oxide, and reappear on evaporating the solution. (Wertheim.)

b. Crystals with 1 *At. Water.* Separate from a more dilute solution cooled below + 10°. Square-based octohedrons with predominant *p*-face. (Fig. 24.) At 100°, they give off $\frac{1}{3}$, and at 275°, the remaining $\frac{2}{3}$ of their water of crystallization, assuming at the same time a yellowish red colour. They are much less soluble in water than uranic nitrate. (Wertheim, *J. pr. Chem.* 29, 209.) This salt appears likewise to have been obtained by Klaproth & Richter, according to whom it forms transparent, topaz-coloured square prisms with four-sided summits; they are permanent in the air, and sparingly soluble in water.

	Crystals (*a*).		Péligot.	Wertheim.
U^2O^3	144	67·61	67·30	67·24
$C^4H^3O^3$	51	23·94		23·95
2 Aq	18	8·45		8·32
$C^4H^3(U^2O^2)O^4 + 2Aq$	213	100·00		99·51

Crystals (b).			Wertheim.
U^2O^3	144	64·86	64·57
$C^4H^3O^3$	51	22·98	23·55
3 Aq	27	12·16	12·40
$C^4H^3(U^2O^2)O^4 + 3Aq$	222	100·00	100·52

The carbon in the salt *a* amounts to 11·28 p. c. (Péligot, *Compt. rend.* , 735; also *J. pr. Chem.* 23, 494.)

Acetate of Uranic oxide and Ammonia. — Obtained by adding carnate of ammonia to a hot solution of uranic acetate, till a uranic comund begins to separate; redissolving this compound in acetic acid; d leaving the evaporated solution to crystallize by cooling. An excess acetic acid or acetate of ammonia is rather useful than hurtful. — Or adding carbonate of ammonia to a boiling solution of uranic acetate l the whole of the uranic oxide is precipitated, redissolving the precipite in acetic acid, and cooling the solution. — Thin, yellow, silky needles nich slightly redden litmus-paper, give off 10·38 p. c. of water at 100°, ssolve readily in water, and are not decomposed by it at a boiling heat. Vertheim.)

Crystallized.			Wertheim.
NH^4O	26	4·99	
2 U^2O^3	288	55·28	55·14
3 $C^4H^3O^3$	153	20·37	29·62
6 Aq	54	10·36	10·38
$NH^3,C^4H^4O^4 + 2[C^4H^3(U^2O^2)O^4] + 6Aq$	521	100·00	

Acetate of Uranic oxide and Potash. — Prepared in a similar manr. Yellow square prisms with four-sided summits. *Fig.* 30 ; $e : e$ on e farther side of the axis = 57° 39′; $e : r$ = 151° 10·5′. — Gives off its ater at 275°, assuming a yellowish red colour. When heated to redness the air, it leaves uranate of potash. Dissolves readily in cold water, nd deposits some of the uranic oxide when the solution is boiled. Vertheim.)

Crystallized.			Wertheim.
KO	47·2	9·32	9·22
2 U^2O^3	288·0	56·89	56·27
3 $C^4H^3O^3$	153·0	30·23	30·00
Aq	18·0	3·56	3·74
$C^4H^3KO^4,2[C^4H^3(U^2O^2)O^4] + 2Aq$	506·2	100·00	99·23

Acetate of Uranic oxide and Soda. — First obtained by Duflos. — Prepared ke the ammonia double-salt. Regular tetrahedrons, whose summits are uncated with the faces of a rhombic dodecahedron. Anhydrous. When nited in the air, it leaves 67·53 per cent. of yellow uranate of soda. Wertheim.)

Crystallized.			Wertheim.
NaO	31·2	6·61	6·44
2 U^2O^3	288·0	60·99	60·36
3 $C^4H^3O^3$	153·0	32·40	31·88
$C^4H^3NaO^4,2[C^4H^3(U^2O^2)O^4]$	472·2	100·00	98·68

Acetate of Uranic oxide and Baryta. — Prepared in a similar manner. mall yellow spangles easily soluble in water; at 275° they give off their

jelly, which, when diluted with water, deposits a very basic salt in the form of a loose powder. (Schindler.)

Zinco-uranic Acetate. — Prepared like the corresponding ammonia-salt. Light yellow crystals, which at 250°, give off their water and assume a dingy yellow colour, and at a red heat, leave a mixture of uranate of zinc and uranaso-uranic oxide, because part of the zinc is reduced by the charcoal and volatilized. Baryta-water added to the aqueous solution throws down uranate of zinc. (Wertheim.)

	Crystallized.		Wertheim.
ZnO	40	7·87	7·79
$2\ U^2O^3$	288	56·70	56·50
$3\ C^4H^3O^3$	153	30·12	29·43
3 Aq	27	5·31	5·88
$C^4H^3ZnO^4,2[C^4H^3(U^2O^2)O^4]+3Aq$	508	100·00	99·60

Acetate of Cadmium. — Small prisms, generally collected in stellate groups, tolerably permanent in the air and very soluble in water. (Stromeyer.) According to Meissner and John, the salt is not crystallizable, but leaves a gelatinous mass when evaporated.

Stannous Acetate. — The boiling acid dissolves the metal but slowly, with evolution of hydrogen; the hydrated protoxide it dissolves readily; the salt is also formed by decomposing aqueous protochloride of tin with sugar of lead. The solution evaporated to a syrupy consistence (and covered with alcohol, according to Berzelius), yields small, firm, transparent, and colourless crystals (Lemery, Morveau); it absorbs oxygen greedily and deposits stannic oxide. (Hausmann, *Scher. J.* 2, 528.)

Tinfoil continuously digested with strong acetic acid yields, without evolution of gas, first a yellow and then a brown solution. This solution remains unaltered in the dark, even if the air has access to it, so that a pure stannous salt crystallizes from it. But if exposed to sunshine, even in glass tubes completely filled with the solution, it becomes paler, and at the end of 2 or 3 weeks perfectly colourless, the decomposition in the sealed tubes being merely slower than in vessels exposed to the air; it then consists of pure stannic acetate, and therefore no longer produces a purple colour with solution of gold. (N. Fischer, *Kastn. Arch.* 9, 347.)

Stannic Acetate. — The solution yields by evaporation a yellowish, gummy mass. (Wenzel.)

Bichloride of Tin forms a crystalline compound with *glacial acetic acid.* (Wenzel.)

Acetate of Lead. — *a. Sexbasic.* — 1. Obtained by precipitating lead-vinegar (p. 314,) with very large excess of ammonia. (Berzelius, *Ann. Chim.* 94, 298.) — According to Payen (*Ann. Chim. Phys.* 65, 239, and 66, 37), solution of sugar of lead forms with ammonia needles of the terbasic salt; and when its aqueous solution is mixed with ammonia in any proportion whatever, hydrated oxide of lead separates out, or at high temperatures the anhydrous oxide. — According to Liebig, (*Chim. org.*), however, this supposed hydrated oxide obtained by Payen is really the sexbasic acetate; for when it is subjected to dry distillation, carbonic

acid and acetone are evolved without blackening, and yellow oxide remains behind. — According to Behrens (*N. J. Pharm.* 4, 18) a solution of sugar of lead, strongly supersaturated with ammonia, separated by filtration from any carbonate of lead that may fall down, and then placed in the dark, yields in a few days, crystals containing 5 At. oxide of lead to 1 At. acetic acid.

2. Potash in excess, which throws down pure yellow oxide of lead from a boiling solution of the neutral acetate, forms, at all temperatures below 100°, a white precipitate which does not give off acetic acid when heated with sulphuric acid, but when subjected to dry distillation, yields an empyreumatic liquid and leaves a mixture of oxide and metal. (Winkelblech, *Ann. Pharm.* 21, 27.)

3. The solution of sugar of lead, or even that of the less basic salts, agitated with excess of oxide of lead, or heated, deposits the sexbasic salt in the form of a bulky powder and scum. — Basse (*N. Gehl.* 5, 126) boils 1 pt. of sugar of lead dissolved in water with 2 pts. litharge; and Döbereiner (*Schw.* 17, 257), the solution of 1 At. sugar of lead with 3 At. oxide of lead. When the aqueous solution of the terbasic salt is boiled with excess of sugar of lead, the same salt is deposited, and the liquid then retains scarcely any lead. (Mitscherlich.) — According to Kühn, no sexbasic salt is produced in this process: 10 pts. of sugar of lead agitated for a while with 14 pts. oxide of lead and 96 pts. hot water in a close vessel and then set aside, change in the course of an hour into a white tenacious mass, which, when diluted with water and washed with thoroughly boiled water out of contact with the air, leave on the filter 8·08 pts. of a white deposit, which, however, when treated with sulphuric acid yields a quantity of sulphate of lead containing nearly 8·08 pts. of oxide. Hence the white deposit cannot contain more than a trace of acetic acid, but consists of oxide of lead mixed with a small quantity of carbonate. (Kühn, *Schw.* 61, 236.) — In Kühn's process, there remains, after several hours' digestion, only 2·84 pts. of white deposit, which yields with sulphuric acid 3·08 pts. sulphate of lead containing 2·24 pts. of oxide; hence these 2·84 pts. of white deposit do not consist of pure oxide of lead. It appears, therefore, that 10 pts. sugar of lead have dissolved $14 - 2{\cdot}24 = 11{\cdot}76$ pts. of oxide of lead; — $10 : 11{\cdot}76 = 190 : 222{\cdot}4 =$ 1 At. : 2 At. Consequently a solution of terbasic acetate has been formed. (Liebig, *Mag. Pharm.* 35, 124.) — There is, doubtless, formed in this process a consderable quantity of terbasic salt, which, together with the sexbasic salt, forms the white deposit, but may be extracted by washing with water more completely as the process is longer continued. Perhaps Liebig continued this washing for a longer time, so that all the terbasic salt was dissolved and only the sexbasic remained; but if that be the case, it is the more difficult to understand how Kühn, in the white deposit obtained by him, which was so large in quantity and must therefore have contained a considerable amount of terbasic salt, could have found nearly 100 per cent. of oxide of lead. Wittstein also (*Repert.* 84, 181), denies the existence of a sexbasic salt.

When 1 part of acetate of soda is boiled for half an hour with 3 pts. of finely pulverized litharge and with water, only $\frac{1}{66}$ of the soda is set free, and the slightly alkaline liquid contains only a trace of lead. (Anthon, *Repert.* 76, 223.) In this case there is perhaps formed a small quantity of sexbasic acetate.

White powder, but slightly soluble in boiling water, and separating therefrom in needles having a silky lustre. At 212° C. in vacuo, it gives off 3 per cent. of water and becomes reddish. (Berzelius.) Absorbs carbonic acid rapidly from the air. (Mitscherlich.)

Crystallized.			Berzelius.
6 PbO	672	89·60	91·3
$C^4H^3O^3$	51	6·80	5·7
3 Aq	27	3·60	3·0
$5PbO,C^4H^3PbO^4+3Aq$	750	100·00	100·0

b. Terbasic or *Trisacetate.*—1. Obtained by saturating an aqueous solution of sugar of lead with oxide of lead, and separating the terbasic salt from the filtrate.—*a.* 1 pt. of sugar of lead is digested with 1·2 pts. of litharge and with water; the filtrate mixed with alcohol; and the resulting precipitate washed with alcohol, then dried in vacuo over oil of vitriol, and preserved in such a manner as to protect it from the action of carbonic acid. (Berzelius, *Ann. Chim.* 94, 299.)—*b.* 1 pt. of sugar of lead is boiled for half an hour with 2 pts. of oxide and 10 pts. of water, and the filtrate set aside in a closed vessel; after two days it deposits white opaque points, which appear under the microscope to be composed of transparent needles; a still larger quantity is obtained by evaporating the filtrate in a place where no carbonic acid can have access to it, and more yet on adding half a measure of alcohol or better of wood-spirit. (Payen.)

2. By precipitating a solution of sugar of lead with ammonia.—A solution of sugar of lead supersaturated with ammonia and filtered, deposits in a few hours shining needles of the terbasic salt. When a solution of sugar of lead is precipitated by ammonia and the precipitate dissolved by adding water and heating, the same needles separate as the liquid cools. If the sugar of lead is dissolved in alcohol, the ammonia forms so copious a precipitate that the mixture solidifies; it consists of microscopic needles, disappears when the whole is heated, and separates again in larger needles on cooling. These needles are free from ammonia. (Payen, *Ann. Chim. Phys.* 65, 239.) The following mode of preparation is recommended by Payen: Mix 5 measures of aqueous sugar of lead solution saturated at 30°, with 5 measures of water completely freed from carbonic acid by boiling; and to this mixture, whose temperature is 80°, add a mixture of 1 measure of aqueous ammonia and 5 measures of water at 70°. As the liquid cools, the salt separates in numerous fine needles; the mother-liquor mixed with an equal quantity of alcohol or wood-spirit, yields more crystals of the same salt.—The concentrated solution of sugar of lead may also be precipitated by ammonia; the precipitate, which consists of fine needles, boiled with water; and the filtrate left to crystallize by cooling.—The salt separates most beautifully from the hot liquid containing acetate of ammonia; hence the second process yields finer needles than the first.—The crystals must be washed out of contact of air, pressed between paper, and dried in vacuo. (Payen.)

Delicate, shining, transparent needles, which do not effloresce in vacuo at 15°, but give off their 1 At. water when heated to 100° in vacuo. (Payen.) They cannot be fused without decomposition. The crystals dissolve in 5·56 pts. of boiling water. Ammonia, added to the

solution in any proportion, throws down hydrated oxide of lead at ordinary temperatures, and the anhydrous oxide at a boiling heat; the precipitation is prevented by the presence of acetate of ammonia. The crystals also dissolve in hydrated alcohol or wood-spirit, slightly also in wood-spirit of 97 per cent., but not in alcohol of 96 per cent.; both liquids also cause the separation of needles from the aqueous solution. (Payen, *Ann. Chim. Phys.* 66, 37; also *J. pr. Chem.* 13, 474.) — The salt reddens turmeric and turns violet green; its taste is less sweet than that of sugar of lead. It is rapidly decomposed by carbonic acid. (Berzelius.)

Crystals dried at 15° in vacuo.			Payen.	Berzelius.
3 PbO	336	84·85	85·00	86·77
4 C	24	6·06	6·40	
4 H	4	1·01	0·99	
4 O	32	8·08	7·61	
$2PbO,C^4H^3PbO^4+Aq$	396	100·00	100·00	

According to Berzelius the salt is anhydrous.

Bibasic or *Di-acetate.* — The boiling aqueous solution of 1 At. sugar of lead is capable of dissolving 1 At. oxide of lead. (Döbereiner, *Schw.* 17, 257.) 190 pts. sugar of lead and 95 pts. oxide digested together in water, leave only 0·62 pts. of insoluble residue, consisting of carbonate of lead. When the oxide is in excess, a white deposit is left, and a solution is formed containing only 2 At. oxide of lead to 1 At. acid. (Kühn, *Schw.* 81, 236.) [Compare, however, the opposite statement by Liebig, p. 311.]

190 pts. (1 At.) of sugar of lead dissolved in water are mixed with 112 pts. (1 At.) of litharge, previously freed from carbonic acid by gentle ignition and pulverized. — On boiling, the mixture first becomes white and thick from formation of a large quantity of terbasic salt, which is then slowly converted, in the cold, into bibasic salt and dissolves; if the mixture be agitated for 3 or 4 hours in the cold, the quantity of white deposit formed is much smaller, and subsequently dissolves. If we proceed in this manner with 190 pts. of sugar of lead, 112 pts. of oxide, and 224 pts. water, we obtain a solution which cannot be filtered and must therefore be clarified by setting it aside for a week and then decanting; if it be then mixed with twice or four times its volume of alcohol, the bibasic salt separates from it in crystals, in an interval varying from 1 to 24 hours. The decanted solution evaporated out of contact of air soon becomes covered with saline films; if it be further evaporated at 50°, there remains a mass which appears moist while warm but dry when cold, contains 6 per cent. (2 At.) water, softens between 60° and 70°, and afterwards becomes dry and hard, giving off 2·9 per cent. (1 At.) of water. This mass, if subsequently heated above 100°, gives up all its water. The crystals [containing 2 At. water?] also lose their lustre above 100°, and then fuse into a dull, white, saline mass. (Schindler.)

From the mass evaporated at 50° (containing 2 At. water), any sesquibasic salt that may be mixed with it is easily extracted by alcohol. If it be first dehydrated and then treated in the state of powder with alcohol, the mixture passes milky through the filter; but on heating it to the boiling point, the undissolved portion again assumes the crystalline aspect of the bibasic salt, and the liquid filters easily. (Schindler.)

The concentrated aqueous solution causes filter-paper (also the

cuticle) to swell considerably and does not pass through; but the solution of 1 pt. of the salt in $1\frac{1}{2}$ pts. water filters very easily. — This salt, as well as the trisacetate, produces red and yellow colours with many oils both fixed and volatile. (R. Schindler, *N. Br. Arch.* 41, 129.)

Thénard (*A. Gehl.* 1, 335) obtained the same salt in crystalline laminæ from the liquid produced by boiling 2 pts. of sugar of lead with 3 pts. of lead-oxide.

Dried at 100°.			Schindler.
2 PbO	224	81·46	81·22
$C^4H^3O^3$	51	18·54	18·69
$PbO,C^4H^3PbO^4$	275	100·00	99·91

Dried at 70°.			Schindler.
2 PbO	224	78·87	78·62
$C^4H^3O^3$	51	17·96	18·11
Aq	9	3·17	
$PbO,C^4H^3PbO^4,+Aq$	284	100·00	

Dried at 50°.			Schindler.	Thénard. *Crystallized.*
2 PbO	224	76·45	75·88	78
$C^4H^3O^3$	51	17·41	17·49	17
2 Aq	18	6·14		5
$PbO,C^4H^3PbO^4+2Aq$	293	100·00		100

Payen appears not to admit the existence of a bibasic salt, inasmuch as he does not mention it.

Lead-vinegar, Bleiessig, Acetum Saturni s. *Lythargyri,* and in the concentrated state, *Extract of Lead, Blei-extract, Extractum Saturni,* as prepared according to the directions commonly given, must be regarded as an aqueous solution of diacetate of lead, which, according to the proportion of oxide which has been digested with the acetic acid or the neutral acetate of lead, likewise contains terbasic and sesquibasic acetate.

The oxide of lead commonly used in the preparation is finely pulverized litharge. As this substance generally contains copper, the lead-vinegar prepared from it is also contaminated with copper. This metal may be removed, either by adding lead-foil or lead-filings to the litharge, on which the liquid containing acetic acid is to act, whereby the greater part of the copper is reduced; or, according to Bischof, by placing the litharge for a day in contact with a solution of carbonate of ammonia amounting to $\frac{1}{10}$ of the litharge, and shaking up the mixture frequently, then filtering and washing. (V. 109.) — The litharge may be entirely freed from carbonic acid by gentle ignition.

Lead-vinegar was formerly prepared by boiling down crude or distilled vinegar with excess of litharge, and filtering. At present, the aqueous solution of sugar of lead is more or less saturated with litharge, sometimes by placing the materials together either warm or cold in a stoppered bottle, sometimes by boiling, or by gradually adding the litharge to the hot solution of sugar of lead.

If, according to the *Pharm. Badensis,* we take 222 pts. (2 At.) lead-oxide to 190 pts. (1 At.) sugar of lead, a white deposit of sexbasic salt *is left,* the filtrate gives a copious precipitate with absolute alcohol, and

contains only 2 At. lead-oxide to 1 At. acetic acid. — With 190 pts. (1 At.) sugar of lead to 95 pts. ($\frac{5}{7}$ At.) oxide, according to the *Pharm. Boruss.*, the quantity of white deposit left undissolved is smaller. Lead-vinegar thus obtained contains bibasic acetate with a small quantity of sesquibasic salt. — With 190 pts. (1 At.) sugar of lead to 63 pts. (somewhat more than $\frac{1}{2}$ At.) oxide, according to the *Pharm. Bavar.* and *Gallica*, the quantity of white sediment left is very small. This lead-vinegar, which consists chiefly of sesquibasic acetate, may be mixed with an equal quantity of absolute alcohol without producing a precipitate, and is capable of dissolving a still larger quantity of oxide of lead. (J. A. Büchner, *Repert.* 81, 295.)

The solution of 3 pts. sugar of lead in 15 pts. water, has a density of 1·111: if (according to the *Pharm. Bavar.*) 1 pt. of lead-oxide be dissolved in it at 25°, with agitation, the decanted liquid has a density =1·155: with $2\frac{1}{2}$ pts. oxide (*Pharm. Boruss.*) it is 1·170; with 3·5 oxide (*Pharm. Badens.*) it is 1·232; and with 4·5 oxide (according to Dumas), a thick magma is formed.

These considerations have induced Büchner and Berzelius (*Jahresber.* 24, 222,] to agree with Döbereiner's view (*Schw.* 17, 257), that the best proportion for the preparation of lead-vinegar is 190 pts. (1 At.) sugar of lead to 112 pts. (1 At.) oxide of lead (or perhaps 2 : 1) inasmuch as when a larger quantity of oxide is used, sparingly soluble basic salts are formed.

Lead-vinegar is a colourless or occasionally a yellowish liquid, which when very highly concentrated has a density exceeding 1·28. It reddens turmeric after a while, and gives a precipitate with carbonic acid, the precipitation going on till a very acid salt remains in solution; hence it becomes turbid even on the addition of distilled water, if the water has not been thoroughly freed from carbonic acid by boiling. Lead-vinegar exposed to sunshine deposits carbonate of lead [from decomposition of acetic acid?] J. Davy (*N. Edinb. Phil. J.* 6, 126.)

Sesquibasic. — 1. Formed by heating dehydrated sugar of lead till it melts, then more strongly till it boils, gives off $\frac{1}{3}$ of its acid (in the decomposed state), and suddenly solidifies to a greyish white mass of the sesquibasic salt. (Matteucci, *J. Chim. méd.* 7, 419.) — The aqueous solution of this residue evaporated to a syrup out of contact of air, yields the salt after a while, crystallized in nacreous laminæ. (Wöhler, *Ann. Pharm.* 29, 63.) — 2. By digesting the aqueous solution of 190 pts. (1 At.) sugar of lead, with 56 pts. ($\frac{1}{2}$ At.) of finely pulverized oxide of lead free from carbonic acid till it dissolves, and evaporating the filtrate in vacuo over oil of vitriol till it crystallizes. — 3. A solution of 396 pts. (1 At.) of the terbasic salt, and at most 190 pts. (1 At.) of sugar of lead, is quickly evaporated to a small bulk, and left to cool in a stoppered bottle for four days; — after which the resulting crystals are separated by a press from the syrupy mother liquor; dried between paper; then pulverized and more completely dried in vacuo at 100°; dissolved in absolute alcohol to free them from any terbasic [or bibasic?] salt that may be present in excess; and the solution, after filtration, evaporated to the crystallizing point. (Payen.)

In the dry state, this salt forms a white amorphous mass, which, when strongly heated, gives off acetone together with a large quantity of carbonic acid. (Matteucci.) White, porous mass. (Wöhler.) In the hydrated crystallized state, it forms transparent, colourless, shining,

six-sided tables and laminæ, which have an alkaline reaction, are less altered by exposure to the air than sugar of lead, do not give off water or acid in vacuo over oil of vitriol, and when heated give off their water and melt. (Payen.)

The crystals dissolve at 12·75° in 0·9 pt. water, therefore more abundantly than sugar of lead. The solution is capable of dissolving both terbasic and monobasic acetate, whereby it acquires a syrupy consistence and loses its crystallizing power. A solution saturated in the cold yields crystals of sugar of lead on the addition of a few drops of acetic acid, and forms terbasic acetate when digested with oxide of lead. Carbonic acid throws down carbonate of lead from it. A small quantity of ammonia throws down the terbasic acetate; a larger quantity precipitates hydrated oxide of lead, or from a hot solution, the anhydrous oxide. (Payen.)

In alcohol, the crystals dissolve less freely than in water, but more easily than sugar of lead; and the cold saturated aqueous solution is not precipitated by an equal volume of alcohol. The salt crystallizes more beautifully from hot, slightly hydrated alcohol, than from water. (Payen, *Ann. Chim. Phys.* 66, 37; also *J. pr. Chem.* 13, 474.)

According to R. Schindler (*N. Br. Arch.* 41, 129), the saturated aqueous solution mixed with from half to twice its bulk of alcohol yields the salt in nacreous laminæ, containing 2 At. water, melting and giving off 2 per cent. (1 At.) of water at 90°, and solidifying on cooling to a colourless gum, which, when more strongly heated, gives off its second atom of water and is converted into a white saline mass.

Dehydrated.			*Crystallized.*			Payen.	Schindler.
3 PbO	336	76·71	3 PbO	336	75·17	74·91	75·34
2 $C^4H^3O^3$	102	23·29	2 $C^4H^3O^3$	102	22·82		22·60
			Aq	9	2·01		
$PbO,2(C^4H^3PbO^4)$	438	100·00	+ Aq	447	100·00		

On the subject of the basic acetates of lead, *vid.* also Wittstein. (*Repert.* 84, 181.)

Monobasic or *Neutral Acetate.* — *Sugar of Lead, Bleizucker, Saccharum Saturni.* — Prepared on the large scale by causing distilled wine-vinegar or cider-vinegar, or purified wood-vinegar, to act upon oxide of lead, or with access of air, upon metallic lead. — The vapour of the vinegar is passed under litharge, till the latter is dissolved up in the form of a neutral compound, — during which action part of the water evaporates — and the resulting liquid is left to cool to the crystallizing point without further evaporation. (Gentele.) — Or, the vinegar is heated in a copper boiler with a few plates of lead, which prevent, by galvanic action, the solution of the copper, and precipitate the copper which is dissolved out of the litharge; more litharge or impure white lead, &c., is then added in such proportion as to form lead-vinegar; the solution decanted, evaporated, and mixed with a sufficient quantity of acetic acid to make it redden litmus, then strained through a conical bag, and left to crystallize. The mother-liquor, evaporated and mixed with acetic acid, yields an additional quantity of crystals, and so on several times. 1 pt. of litharge yields about 1½ pt. sugar of lead. (Mitscherlich.) — Or, strong distilled vinegar is poured upon small pieces of lead contained in tubes, the liquid from the first tube run off to a second also filled with lead, thence into a third, &c., — then

again into the first, the lead in which has had time to oxidize again in the air, and form sugar of lead with the adhering acetic acid, — then once more upon the second, &c., till the vinegar is sufficiently saturated with lead. (Bérard.) Similar, in short, to the preparation of blue vitriol. (VI., 428.) — Or, lead in small pieces is placed in shallow dishes half filled with distilled vinegar, exposed for a long time to the air, and frequently turned.

The commercial crystals, which have carbonate of lead and also brown matter adhering to them, are purified by solution in hot water containing a small quantity of distilled vinegar, the solution thus formed being subsequently filtered and cooled to the crystallizing point.

If they be deprived of their water of crystallization by leaving them in vacuo over oil of vitriol (Berzelius), or by fusing them at a gentle heat, stirring all the while (Mitscherlich), or by heating them in a retort to a temperature above 100°, (Matteucci), the anhydrous salt remains in the form of a white pulverulent or compact mass, which if heated to its melting point and then cooled, solidifies at 192° to a coarsely crystalline mass, and, according to Payen, may be obtained in anhydrous six-sided tables by solution in boiling absolute alcohol and cooling.

Dehydrated sugar of lead heated in a retort is completely converted at 280° into a clear liquid; boils for a while with evolution of acetic acid and a small quantity of acetone; assumes a brownish tint; and if the heat be gradually raised to 656° [?], suddenly solidifies in the form of a white crystalline mass of sesquibasic acetate, which afterwards at a still higher temperature, gives off the remaining $\frac{2}{3}$ At. of the acetic acid in the form of acetone and carbonic acid. (Matteucci, *J. Chim. méd.* 7, 419; *Schw.* 63, 236.) The products evolved in the conversion of sugar of lead into the terbasic [sesquibasic?] salt, are not acetic acid with a little acetone, but acetone and carbonic acid:

$$6C^4H^3PbO^4 = 2(PbO,2C^4H^3PbO^4) + C^6H^6O^2 + 2CO^2.$$

The residue contains also a small quantity of carbonate of lead as a secondary product. (Wöhler, *Ann. Pharm.* 29, 63.) — Döbereiner had stated (*Schw.* 17, 256) before Matteucci, that 100 pts. of sugar of lead subjected to dry distillation give off acetic acid and acetone, with ebullition, and are converted after a while into 85·84 pts. of basic salt, which, when more strongly heated, is resolved into carbonic acid and marsh-gas, acetone with a small quantity of acetic acid, and a non-coherent grey residue, amounting to 66·02 pts.; this residue acquires the metallic lustre when rubbed upon the polishing stone, and consists of 63·78 pts. lead, and 2·24 charcoal. — The dry salt heated in the air melts with appearance of fire, and afterwards solidifies, resolving itself into a mixture of lead-oxide and metallic globules. Paper saturated with sugar of lead or lead-vinegar, and then dried, burns like tinder when set on fire.

¶. When an intimate mixture of 2 pts. perfectly dehydrated sugar of lead and 1 pt. of the so-called Paris blue (VII, 437), also perfectly dry, is gently heated, a large quantity of gas is given off (consisting probably of 2 vol. carbonic acid to 1 vol. carbonic oxide), and at the same time an ethereal distillate passes over; afterwards, at a red heat, a yellow oil distils over, a large quantity of carbonate of ammonia is evolved, and a pyrophoric residue is left. The ethereal distillate mixes with water, ether, and alcohol in all proportions; it appears to be a mixture of acetone and acetonitryl, C^4H^3N, (Löwig & Schweizer, *Ann. Pharm.* 75, 350.) ¶.

Dehydrated in vacuo.			Berzelius.	Payen.
PbO	112	68·71	68·52	68·87
4 C	24	14·72	14·75	14·38
3 H	3	1·85	1·99	1·86
3 O	24	14·72	14·74	14·89
$C^4H^3PbO^4$	163	100·00	100·00	100·00

From the aqueous solution, the salt separates combined with 3 At. water in the crystals in which it commonly occurs. A solution of the previously dehydrated salt in dilute alcohol also yields crystals containing 3 At. water. (Payen.) — Transparent and colourless prisms belonging to the oblique prismatic system. *Fig.* 106; cleavage parallel to *t* and *i*. $u : u' = 128°$; $u : t = 116°$; $i : u = 93° 30'$; $i : t = 109° 32'$. (Brooke, *Ann. Phil.* 22,374.) According to Mitscherlich, it is isomorphous with the acetates of baryta and strontia. — Sp. gr. 2·575. (Thomson.) — Tastes astringently sweet. Turns violets green. (Morveau.) The aqueous solution turns violets green, even after carbonic acid has been passed through it long enough to cause it to redden litmus; the crystals do not redden litmus unless they have been separated from a very acid solution. (Walchner.)

With Water of Crystallization.			Berzelius.	Thénard.	Döbereiner.	Thomson. *a.*	Thomson. *b.*
PbO	112	58·95	58·71	58	62	59·26	59
$C^4H^3O^3$	51	26·84	26·97	26	28	24.46	22
3 Aq	27	14·21	14·32	16	10	14·28	19
$C^4H^3PbO^4 + 3Aq.$	190	100·00	100·00	100	100	100·00	100

Berzelius. (*Ann. Chim.* 94, 298.) Thénard. (*A. Gehl.* 1, 335.) Döbereiner, *Schw.* 17, 256.) — Thomson (*Ann. Phil.* 14, 382; 18, 142) regards the salt *a* as the true sugar of lead; the salt *b* [the crystals of which, however, as described by him, agree perfectly with those of sugar of lead] he regards as a peculiar salt = PbO, $4C^4H^3PbO^4 + 19$ Aq.

Crystallized sugar of lead effloresces slightly in warm dry air, giving off water and acetic acid, and absorbing carbonic acid. Unless the air is completely saturated with moisture, no carbonic acid is taken up, even if acetic acid escapes. (Hochstedter, *J. pr. Chem.* 26, 338.) In vacuo over oil of vitriol, or at temperatures above 40° in the air, it gives up all its water. In vacuo over oil of vitriol, even at 0°, the crystals lose all their water in 8 days but no acid; at 22°, they are completely dehydrated in 48 hours, and if then kept for a longer time in vacuo, lose also a small quantity of acid. (Payen.) — Absolute alcohol frequently renewed deprives the crystals of all their water, so that the residue, dissolved in a fresh portion of boiling absolute alcohol, yields on cooling, crystals of the anhydrous salt. (Payen.) — The hydrated salt melts at 75·5° (Matteucci), and on cooling solidifies after some time in a radiated mass. (Marx, *J. pr. Chem.* 22, 143.) At a heat gradually rising to 100°, it gives off its water with ebullition (but no acid), and then solidifies at that temperature in the form of the anhydrous salt. (Matteucci.) — When the aqueous solution is boiled, part of the acetic acid goes off with the water. (Völckel, *Pogg.* 58, 141.) The solution when exposed to the air is resolved into acetic acid which escapes, and carbonate of lead which is precipitated. (Hochstedter; *comp.* Denot, *J. Pharm.* 20, 8.) — Carbonic acid gas passed through the aqueous solution throws down the greater part of the lead in the form of carbonate, the quantity of lead remaining in solution being smaller as the liquid is more dilute. The solution of 100 pts. sugar

of lead in [how much?] water, deposits, when carbonic acid is passed through it, 45·65 pts. of oxide of lead in the form of 54·68 pts. of carbonate free from acetic acid, so that only 13·3 pts. of oxide remain in solution. The liquid does not dissolve any of the carbonate of lead, so long as it remains saturated with carbonic acid; but after the carbonic acid has been expelled, the carbonate of lead dissolves. On distilling the liquid, acetic acid passes over; and the remaining liquid, which reddens litmus but slightly, yields a fresh precipitate when carbonic acid is passed through it. (Walchner, *Schw.* 48, 257.) — From a solution of 100 pts. sugar of lead in 500 pts. water, carbonic acid gas throws down only 15·98 pts. oxide (in form of carbonate); but with 1300 parts of water, the quantity of oxide precipitated amounts to 39·64 pts.; with 2100 pts. water, to 38·87; and with 3000 pts. water, to 40·54 pts. It appears then that if the quantity of water exceeds 13 times that of the sugar of lead, a further addition of water does not produce any considerable increase in the quantity of lead precipitated. Similarly, 100 parts of moderately strong acetic acid placed in contact at ordinary temperature with an excess of carbonate of lead, dissolve 29·32 pts. of oxide; but the same quantity of acid diluted with 800 pts. of water dissolves only 20·02 pts., and with 1600 pts. water, only 16·26 pts. of oxide. (G. Bischof, *J. pr. Chem.* 7, 181.)

A solution of 1 pt. sugar of lead in 8 to 16 pts. water is not precipitated by ammonia, baryta-water, or lime-water, provided carbonic acid be completely excluded. (Bucholz, *A. Gehl*, 5, 254). When a solution of sugar of lead is dropped into excess of ammonia, white hydrated lead-oxide is thrown down in the cold, and at higher temperatures, sometimes the hydrate, sometimes the crystallized anhydrous oxide. When 1 pt. of an aqueous solution of sugar of lead, saturated at 22°, is mixed with 2 pts. water, and ammonia added by drops till the liquid smells slightly of it, the mixture remains clear, but after a few hours deposits acetate of lead. (Payen.)

¶ Aqueous solution of potash, of sp. gr. 1·06, added by drops and with agitation to a boiling-hot solution of sugar of lead of sp. gr. 1·25 to 1·30, does not for some time produce any permanent precipitate; but suddenly the whole liquid solidifies to a white magma, formed by a double salt, $3PbO,2KO,3C^4H^3O^3$, which is moderately soluble in hot water. (Taddeis, *Raccolta fisico-chimica Italiana*, 2, 562; *Chem. Gaz.* 1848, 169.) ¶

Sulphate of potash added to solution of sugar of lead, throws down a loosely united compound of sulphate of lead and sulphate of potash. The presence of gum retards the precipitation by sulphates. The solution of 1 pt. of sugar of lead in 3000 pts. water is precipitated by sulphate of soda; but if the water also contains in solution $\frac{1}{50}$ of its weight of gum, the precipitate does not show itself when the proportion of sugar of lead in the water is less than 1 pt. in 1000; if the water contains $\frac{1}{30}$ of its weight of gum, the precipitate is not formed even with this quantity of lead, not even when the liquid is boiled or left to itself for a long time; but in that case, a few drops of nitric, hydrochloric, or sulphuric acid produce the precipitation. (Walcker, *N. Quart. J. of Soc.* 3, 376.) The solution of 1 pt. corrosive sublimate in 100 pts. water is not clouded by a small quantity of sugar of lead, but yields a copious precipitate of lead with lead-vinegar. (Buchner, *Br. Arch.* 19, 270.) The precipitate is probably oxychloride of lead. By this test we may readily ascertain whether the sugar of lead contains any basic salt.

Neutral acetate of lead dissolves in 1 pt. of water at 40° (Wenzel); and in about ½ pt. of boiling water. When a solution saturated at 22° is mixed with an equal volume of 95 per cent. alcohol, the clear mixture, after a few days, deposits beautiful prisms; if these do not appear, a crystalline precipitate is instantly formed on agitating the liquid. (Payen.) Sugar of lead dissolves with tolerable facility in alcohol. Ether added to the solution throws down the salt in the form of a crystalline powder. (Döbereiner.) From its solution in alcohol of sp. gr. 0·828, the salt is also partially precipitated in the crystalline form by absolute alcohol. (Reichenbach, *Schw.* 62, 145.)

Minium dissolves abundantly and without decomposition in strong vinegar, forming a colourless liquid, which remains permanent in close vessels, but deposits brown peroxide of lead when exposed to the air, or when evaporated or diluted with water. (N. Fischer, *Schw.* 53, 124.) [Glacial acetic acid is required for this purpose. Peroxide of lead does not dissolve either in glacial acetic acid or in concentrated vinegar.]

Acetate of Uranium and Lead. — A solution of 1 pt. neutral acetate of lead and a somewhat larger quantity of uranic acetate in water containing acetic acid, yields, when somewhat quickly evaporated, pale yellow needles united in tufts, which give off their water of cyrstallization at 275°, leave brown uranate of lead when ignited in the air, and dissolve readily in water. (Wertheim.)

Crystallized.			Wertheim.
PbO	112	27·18	27·14
U^2O^3	144	34·95	34·93
$2\ C^4H^3O^3$	102	24·76	24·94
6 Aq	54	13·11	13·01
$C^8H^3PbO^4,C^4H^3(U^2O^2)O^4 + 6Aq$	412	100·00	100·02

Ferrous Acetate. — Formed by dissolving iron or its sulphide in warm strong acetic acid, not in contact with the air. The concentrated solution yields, on cooling, small, green, sweetish, astringent needles. (H. Davy.) The solution, freed if necessary from ferric oxide by sulphuretted hydrogen with addition of acetic acid in excess and evaporated in a retort, solidifies on cooling to a very pale green mass, consisting of soft silky needles. (Liebig, *Chim. org.*) The dissolved salt oxidizes quickly in the air, and becomes covered with precipitated films of ferric salt. (Wenzel.) These are dark brown, crystalline, and perfectly soluble in water.

Matteucci's statement (*Ann. Chim. Phys.* 52, 136) that the aqueous solution of ferrous acetate is protected by acetate of baryta from precipitation by ammonia, I have not been able to confirm. It is true that part of the ferrous oxide remains in solution; but this is always the case in precipitating by ammonia. (V, 189.)

Ferric Acetate. — *a. Polybasic.* — Precipitated on boiling the dilute solutions of *b* and *c*, in brownish yellow flakes, which, according to Duflos, do not redissolve in strong acetic acid.

b. Monobasic. — 1. This is probably the composition of the dark brown crystalline precipitate deposited by ferrous acetate on exposure to the air, and completely soluble in water.

2. Obtained by saturating cold strong acetic acid with recently precipitated and still moist hydrated ferric oxide. The hydrated oxide, in certain states, is either insoluble or but sparingly soluble in strong acetic acid. According to Trautwein, it is only the terhydrate

$= 3Aq,Fe^2O^3$, which dissolves abundantly in the acid. According to Janssen, it must be precipitated from its solution in hydrochloric or sulphuric acid by neither too small nor too great a quantity of caustic or carbonated alkali; because, in the former case, a basic hydrochlorate or sulphate of ferric oxide will be precipitated, and in the latter, a compound of the hydrate with alkali; both of which are but sparingly soluble in acetic acid. Hence are derived the following methods of obtaining an easily soluble hydrate.

a. 6 pts. of aqueous sesquichloride of iron, of sp. gr. 1·545 (containing 1 pt. of iron) are mixed with 90 pts. of water; then 9 pts. of aqueous potash of sp. gr. 1·333 with 135 pts. water; the iron-solution mixed with exactly two-thirds of the potash-solution; the mixture set aside for a day and shaken now and then, till the light brownish yellow precipitate redissolves and forms a clear dark brown solution; and afterwards the greater part of the remaining third of the potash-solution added, but only in sufficient quantity to produce complete precipitation. The hydrate, after being washed and pressed, amounts to between 3 and 6 parts, and is soluble in 3½ pts. of acetic acid of sp. gr. 1·05 to 1·055. The acid is added to the hydrate in successive portions, each portion being well mixed with it by careful trituration in a basin, the mixture set aside in a glass vessel for 24 hours, and frequently shaken; after which it forms a clear solution, which should be strained through fine linen. If the ferric hydrate and the concentrated vinegar have been mixed, before trituration, with a quantity of water sufficient to bring the solution to 12 parts, the sp. gr. of the solution is between 1·13 and 1·35. (Trautwein, *Repert.* 81, 1.)

β. 1 At. sesquichloride of iron is exactly precipitated by 3 At. carbonated alkali, [*e.g.* 268 pts. 12-hydrated sesquichloride of iron to 430 pts. 10-hydrated carbonate of soda], both solutions being cold and concentrated; the iron-solution added with brisk agitation to the alkaline liquid; and the precipitate carfully washed with cold water. The precipitate obtained from 100 pts. of iron requires 237 pts. of acetic acid of sp. gr. 1·045 to dissolve it completely. [Since, according to page 293, acetic acid of sp. gr. 1·045 contains 34 per cent. of the glacial acid, 237 parts of it must contain 80·58 pts. of glacial acetic acid. This quantity dissolves 100 pts. of iron in the form of 143 pts. oxide; and 143 : 80·58 = 80 : 45·06; consequently, 80 pts. (1 At.) ferric oxide are soluble in 45·06 pts. (¾ At.) glacial acetic acid or 4 At. ferric oxide in 3 At. glacial acetic acid]. If the ferric oxide has been precipitated by an alkaline bicarbonate, the dark brown solution may be kept unchanged; but if the oxide has been precipitated by a caustic alkali or a monocarbonate, the solution becomes turbid in a few days, and solidifies to a stiff jelly; this effect, however, is not due to the presence of silica, but to a residual portion of alkali, which dissolves in the form of acetate, and causes the separation of a basic ferric acetate. But when hydrochlorate of ferric oxide is precipitated by bicarbonate of potash or soda or sesquicarbonate of ammonia, the precipitate contains carbonic acid and does not dissolve in strong acetic acid till it is heated; it then forms with the acid a stiff jelly, which becomes liquid when the carbonic acid escapes; if too much heat be applied, ferric oxide separates and does not redissolve until acted upon by an excess of acetic acid. (Janssen, *Ann. Pharm.* 29, 193.)

γ. A solution of 1 pt. iron in 15 pts. of hot nitric acid of sp. gr. 1·25 is mixed with an aqueous solution of 8 pts crystallized carbonate of soda; the precipitate throughly washed with warm water and squeezed in a

press; the cake, which amounts to between 3·6 and 4 pts. digested with 17 pts. acetic acid of sp. gr. 1·045, and the solution filtered from the undissolved portion. In this process, the hydrated oxide is somewhat in excess, and therefore the saturation is perfect. The filtrate contains 80 pts. (1 At.) ferric oxide to 63·2 pts. (a little more than 1 At.) glacial acetic acid. (Bette, *Ann. Pharm.* 33, 136.)

δ. 6 pts. of aqueous solution of sesquichloride of iron, of sp. gr. 1·5, diluted with 6 pts. water, are mixed with a solution of 9 pts. crystallized carbonate of soda in 20 pts. water, the washed precipitate placed upon a brick, till it is reduced to about 8 pts., and afterwards immersed in 4 pts. of strong acetic acid, and stirred till it is completely dissolved. (Duflos, *N. Br. Arch.* 23, 308.)

ε. Schweinsberg (*Mag. Pharm.* 33, 48) precipitates dilute sesquichloride of iron by caustic soda, added in such proportion that the liquid shall not change the colour either of litmus or of turmeric; washes the precipitate quickly either with hot or with cold water, because its solubility is greatly diminished by continued immersion in the liquid; presses it between blotting-paper as long as the paper is wetted by it; leaves it to dry to a certain degree in warm air; and dissolves it, at 25° to 37°, in strong acetic acid.

The dark red-brown solution of ferric acetate becomes turbid on the addition of acetate of potash, the turbidity appearing immediately or after a time, according to the quantity of the latter, and yields a precipitate which redissolves in pure water: to restore the gelatinous mixture to the liquid state, a large quantity of strong acetic acid is required. (Janssen.) — The solution, when largely diluted with water, is resolved into ferric oxide [polybasic salt ?] which is precipitated, and dilute acetic acid. (Wetzlar, *Schw.* 50, 107.) — This precipitation is accelerated by boiling.

c. Ter-acid. — Formed by precipitating sugar of lead or acetate of baryta with tersulphate of ferric oxide in equivalent proportion, and filtering from the sulphate of lead or baryta; or, according to Pagenstecher, (*Repert.* 73, 38), by adding 17 pts. of completely dry tersulphate of ferric oxide to a solution of 18 pts. acetate of potash in 28 pts. alcohol of sp. gr. 0·85 and 6 pts. water, digesting for 3 days with frequent agitation, straining with pressure through linen, and filtering. — The dark brown solution resembles the preceding, and is also precipitated by dilution and boiling, so as to yield a colourless filtrate free from iron. The same effect is produced on mixing ferric sulphate or other ferric salt with acetate of potash, diluting the dark brown mixture with water, and heating till it begins to boil. (Barker, *Phil. Mag. J.*; also *J. pr. Chem.* 7, 146.) On this reaction is founded a method of separating iron present in the state of sesquioxide from other metals likewise contained in solution. — Ferric acetate is miscible with alcohol.

Cobaltous Acetate. — The red solution yields by evaporation a red residue which turns blue whenever it is heated, and becomes moist on exposure to the air. (Wenzel.) The solution may be used as a sympathetic ink, violet if pure, blue if mixed with common salt. (Ilsemann; *comp.* V. 337.)

Cobaltic Acetate. — Hydrated sesquioxide of cobalt dissolves slowly but completely in strong acetic acid, forming a deep brown-yellow *liquid*, a few drops of which are sufficient to impart a yellow colour to a

considerable quantity of water. The solution sustains a boiling heat without decomposition, but continued exposure to light reduces the sesquioxide of cobalt to protoxide. Sulphuric or nitric acid likewise gradually reduces the sesquioxide to protoxide. (Winkelbech, *Ann. Pharm.* 13, 260.) (For the reactions of this solution, *vid.* V. 328.)

ACETATE OF NICKEL. — Crystallizes apparently in four-sided prisms; apple-green, very sweet. Effloresces on the surface; dissolves in 6 pts. of cold water; insoluble in absolute alcohol. (Tupputi, *Ann. Chim.* 78, 164.)

CUPROUS ACETATE. — First observed by the translator of "Spielmann's Institutions," and by Lassone in the distillation of verdigris; supposed by Proust and A. Vogel to be anhydrous cupric acetate; shown by Gehlen to be cuprous acetate. — According to Berzelius, it often occurs in common verdigris. — This salt sublimes towards the end of the distillation of crystallized verdigris (also of common verdigris, according to Berzelius) in soft, loose, white flakes, which redden litmus and have a caustic astringent taste. (Lassone.) It is composed of $Cu^2O,C^4H^3O^3 = C^4H^3Cu^2O^4$, and does not undergo any change by exposure to moist air. (Berzelius.) According to Gehlen, it becomes moist and green when exposed to the air; and when treated with potash, forms hydrated cuprous oxide. (Gehlen.) — When immersed in water, it is resolved into yellow hydrated cuprous oxide and monobasic cupric acetate, the latter gradually forming and dissolving as the air has access to the liquid. (Berzelius.) It dissolves but partially in alcohol, leaving a yellow powder soluble in ammonia [hydrated cuprous oxide]. (Lassone.)

CUPRIC ACETATE. — *a. With* 48 *Atoms of Base?* Precipitated, on heating the aqueous solution of the sesquibasic salt, in liver-coloured flakes, which towards the end of the washing easily pass through the filter; they are very sparingly soluble in water, and when dry, are black and leave a strong stain. Remains also as an insoluble residue when common verdigris and the terbasic salt are boiled together for a long time; some of the terbasic salt, however, remains mixed with it. (Berzelius.)

	Dried at 65°.		Berzelius.
48 CuO	1920	92·35	92·00
$C^4H^3O^3$	51	2·45	2·45
12 Aq	108	5·20	5·55
$47CuO,C^4H^3CuO^4$	2079	100·00	100·00

b. Terbasic. — 1. Common verdigris is put into cold water, and left to swell up; the pasty mass strained through very porous linen, which retains the impurities of the verdigris, but allows the small crystals of *b* to pass through; the portion which has run through poured upon fine linen (cambric); and the beautiful, light-blue, shining, crystalline scales which remain thereon, pressed and washed with cold water, and finally on a paper filter with alcohol. (Berzelius.) — 2. When ammonia is added to a boiling solution of the monobasic salt till the precipitate is redissolved, and the solution kept for some time at 60°, the salt *b* crystallizes out. (Berzelius.) — 3. The acid of the monobasic salt is imperfectly saturated with ammonia, and the resulting green, non-crystalline jelly, washed first with water which turns it blue, and then with alcohol to prevent it from turning black. (Berzelius.) — 4. When ammonia is

cautiously added, not in excess, to the boiling concentrated solution of the monobasic salt, a heavy, granular, dingy grey-green precipitate is formed, consisting of very small cubical grains. (Berzelius.) — 5. The salt *b* is also formed by digesting the aqueous solution of the neutral salt with hydrated cupric oxide; but it then assumes the form of a beautiful light green, heavy powder. (Proust, Berzelius.)

However different the salt may be in appearance when prepared by these different methods, it has always the same composition. It gives off no water at 100°. When heated, it burns with a slight detonation. (Berzelius.) It is tasteless. When subjected to dry distillation, it gives off a large quantity of water and a small quantity of acetic acid, and leaves the copper partly in the reduced state. It is not decomposed by carbonic acid. Water even at a boiling heat has not the slightest action upon it. (Proust.) When treated with considerable quantities of water, it is completely converted, in the course of a few days, into the neutral salt and brown cupric oxide (Phillips); into the salt *a*. (Berzelius.)

	Dried at 100°.		Berzelius.	Proust.
3 CuO	120·0	65·04	64·36	63
$C^4H^3O^3$	51·0	27·64	27·60	37
$1\frac{1}{2}$ Aq	13·5	7·32	8·04	
$2CuO,C^4H^3CuO^4 + 1\frac{1}{2}Aq$	184·5	100·00	100·00	100

Regarded by Phillips as quadrobasic acetate of cupric oxide.— According to Roux (*Rev. scientif.* 24, 5; abstr. *Ann. Pharm.* 60, 316) the same salt is obtained by boiling the aqueous or alcoholic solution of the monobasic salt, in the form of a blue powder consisting of microscopic needles which contain 9 per cent. of water; therefore $= 2(CuO,HO) + C^4H^3CuO^4$; when heated to 160°, it gives off water and is converted into $2CuO,C^4H^3CuO^4$.

c. Bibasic. — Common blue Verdigris. Prepared on the large scale.— In Montpellier, wine-lees are loosely packed in casks, together with straw, till they pass into the state of acetous fermentation; and when that is ended, they are arranged, in pots covered with straw, in alternate layers with rectangular copper plates heated to 40° (which, when used for the first time, are previously moistened by means of a cloth with a solution of neutral acetate of copper and then dried). At the end of three weeks the plates are taken out, placed in an upright position to dry, dipped 6 or 8 times in water in the course of 6 or 8 weeks, and again left to dry, during which operation the verdigris continually swells up. It is then scraped off; the plates again arranged alternately with fresh sour wine-lees, and the same processes repeated till the plates are corroded. (Chaptal.)— The salt is likewise formed in blue needles when copper plates are exposed for two months to damp air in contact with neutral acetate of copper made up to a paste with water. (Berzelius.) — Delicate, loose, silky, blue crystalline scales and needles, which yield a beautiful blue powder. (Phillips, Berzelius.) The crystals give off 23·45 per cent. of water at 60°, and are converted into a beautiful green mixture of hydrated monobasic and terbasic salt. (Berzelius):

$$2(CuO,C^4H^3CuO^4) = C^4H^3CuO^4 + 2CuO,C^4H^3CuO^4.$$

Blue verdigris mixed with a small quantity of water, forms a paste consisting of small blue crystals and a blue solution. When the paste is repeatedly exhausted with cold water, a solution of monobasic and sesqui-

basic salt runs off, and leaves the terbasic salt, which, becoming continually darker in colour, is ultimately converted into the brown 48-basic salt and a solution of the neutral acetate. (Berzelius.)

$$5(2CuO,C^4H^3O^3) = CuO,C^4H^3O^3 + 3CuO,2C^4H^3O^3 + 2(3CuO,C^4H^3O^3).$$

According to Phillips, the bibasic salt is decomposed by a large quantity of water into terbasic and monobasic salt.

Crystallized.		Berzelius.		Phillips. *French.*	Phillips. *English. In crystals.*	Phillips. *English. Compressed.*
2 CuO	80	43·24	43·34	43·5	43·25	44·25
$C^4H^3O^3$	51	27·57	27·45	29·3	28·30	29·62
6 Aq	54	29·19	29·21	25·2	28·45	25·51
Impurities				2·0		0·62
$CuO,C^4H^3CuO^4 + 6Aq$	185	100·00	100·00	100·0	100·00	100·00

d. Sesquibasic. — 1. Obtained by treating common verdigris with cold water, and leaving the filtrate to evaporate spontaneously, whereupon the sesquibasic salt separates in efflorescences on the edge of the vessel. (Berzelius.) — 2. By adding ammonia in small quantities to the boiling aqueous solution of the neutral acetate, as long as the precipitate redissolves, and leaving the solution to cool. The salt which separates out converts the liquid into a magma, which must be thrown upon a cloth filter, pressed, and washed with alcohol. — The liquid which runs through yields, when mixed with alcohol, an additional quantity of salt in scales, which must also be washed with alcohol. — Delicate bluish crystalline scales, or bluish powder. Gives off from 9·5 to 10·3 per cent. of water (therefore the half, or 3 At.) at 60°, becoming greenish at the same time. Its aqueous solution, at a boiling heat — and if very dilute, even between 20° and 30° — deposits the 48-basic salt, the monobasic salt remaining in solution. (Berzelius.)

			Berzelius.
3 CuO	120	43·48	43·19
$2\ C^4H^3O^3$	102	36·96	36·80
6 Aq	54	19·56	20·01
$CuO,2C^4H^3CuO^4$	276	100·00	100·00

Common Green Verdigris is, according to Berzelius, a mixture of the sesquibasic acetate with small quantities of the bibasic and terbasic salts, and, moreover, frequently contains cuprous acetate, besides impurities; in that case it leaves, when dissolved in distilled vinegar, a residue containing red cuprous oxide [metallic copper?] — In Grenoble this substance is prepared by frequently sprinkling copper plates with vinegar in a warm room; in Sweden, by disposing copper plates in alternate layers with flannel cloths soaked in vinegar, till the verdigris begins to form, then exposing them to the air and frequently moistening them with water.

The greenest kind of common verdigris contains, according to Berzelius:

CuO	49·86
$C^4H^3O^3$	36·66
Aq. and impurities	13·48
	100·00

At 60° it gives off about 10·25 per cent. of water. — Cold water causes it to swell up, leaves undissolved the terbasic salt and the impurities

yields a blue filtrate containing sesquibasic and monobasic salt. Heated with water, it blackens at a lower temperature, in proportion as the quantity of water is greater, but not when boiled in a very small quantity of water. (Berzelius.)

Proust found in common verdigris 60 per cent. of cupric oxide. He at first stated that this substance, when treated with water, is resolved into 43 p. c. of terbasic, and 57 per cent. of monobasic salt; afterwards that it consists of 43 per cent. of monobasic salt, and a hydrate containing 27 p. c. of cupric oxide and 30 p. c. of water. — Destouches (*Bull. Pharm.* 2, 119) supposes common verdigris to contain 30·1 p. c. monobasic acetate, 33·5 cupric oxide, and 36·4 water, together with a small additional quantity of acetic acid.

Jonas. (*N. Br. Arch.* 35, 142; *J. pr. Chem.* 29, 192.)

c. Monobasic, Neutral or *Normal Acetate.* — *Crystallized, Distilled, Purified Verdigris, Verdet, Cristaux de Venus.* — Formed by dissolving cupric oxide or common verdigris in aqueous acetic acid, or by precipitating neutral acetate of lead with sulphate of copper and filtering. In both cases the liquid must be highly concentrated, and then left for some time in a cool place. — The salt crystallizes in combination with water in translucent, dark bluish green prisms belonging to the oblique prismatic system. (*Fig.* 110; cleavage parallel to *i*, *u* and *u'*; $i : u$ or $u' = 105° 30'$; $u : u' = 72°$; $i : f = 119° 4'$; $i : d = 131° 45'$; the *u*- and *u'*-faces often curved. (Brooke, *Phill. Ann.* 6, 39; *comp.* Bernhardi, *Schw.* 4, 23.) The powder has a bright green colour; sp. gr. 1·914. (Gehlen.)

	Crystallized.			Phill.	Ure.	Gehlen.	Berzel.	Proust.
CuO	40	....	40	39·2	39·6	40·15	39·29	39
$C^4H^3O^3$	51	....	51	49·2	52·0	59·85	60·71	61
Aq	9	....	9	11·6	8·4			
$C^4H^3CuO^4 + Aq$	100	....	100	100·0	100·0	100·00	100·00	100

The salt effloresces on the surface. When subjected to dry distillation, it decrepitates, turns brown without melting, yields carbonic acid and a combustible gas, water, acetic acid, and acetone, and towards the end a sublimate of cuprous acetate; the residue is a mixture of copper and charcoal, amounting to about 0·32 .. 0·36. According to Gehlen, the gas evolved contains 6 vol. carbonic acid to 5 vol. carbonic oxide; according to A. Vogel (*J. Pharm.* 1, 339), 4 vol. carbonic acid to 1 vol. carburetted hydrogen. — The distillate amounts to 47, and the residue to 36 per cent. The white sublimate amounts to only $\frac{1}{1210}$ of the verdigris, and being at last carried forward by a liquid [acetone?], contaminates the distillate with copper. (Lassone.) — The greater part of the water goes over at the beginning of the distillation, glacial acetic acid towards the middle, and acetone towards the end; hence the middle distillate has the greatest, and the last the smallest specific gravity, although it saturates more potash than the first. (Derosne, *Ann. Chim.* 63, 267.) — The total distillate formed of these three liquids together, amounts to 50 or 51 per cent. of the crystals. (Gehlen.)

The residue amounts to 31·3 per cent. (Adet), and contains cuprous oxide, besides metallic copper and charcoal. (Adet, *Scher. J.* 2, 174; A. Vogel, *J. Pharm.* 1, 339.) According to Chenevix, it consists wholly of charcoal and copper, without any cuprous or cupric oxide. — The crystals begin to give off acid vapours at 110°, and when heated to 140° yield 9·8 p. c. of tolerably strong vinegar; the residue, which has a fine blue

colour, and still retains its crystalline form, has exactly the composition $C^4H^3CuO^4$, and is perfectly soluble in alcohol. Hence the crystals contain, in addition to the hypothetically anhydrous salt, $C^4H^3CuO^4$, not 1 At. water of crystallization, but a certain quantity of acetic acid; in fact, they only separate from a liquid containing excess of acetic acid. (Gerhardt, *N. J. Pharm.* 9, 50.) — The crystals, after being dried at ordinary temperatures in vacuo over oil of vitriol, do not undergo any further diminution at 100°, but give off 9·6 per cent. of slightly acidulated water between 110° and 140°, afterwards nothing more till they are heated to 240°; from this temperature to 260°, the distillate consists of glacial acetic acid, which by rectification yields 32 per cent. of pure glacial acid; at 270°, white fumes arise which condense into white flakes of cuprous acetate; afterwards a mixture of carbonic acid and combustible gas is evolved. At 330°, the distillation is complete, and a reddish residue is left, consisting chiefly of metallic copper. (Roux, *Rev. scient.* 24, 5; abstr. *Ann. Pharm.* 60, 316.) [No acetone?]

Crystallized verdigris burns in the air with a green flame. (A. Vogel, Berzelius.) — The crystals when immersed in oil of vitriol lose their water and turn white; but after being wiped with paper, recover their blue colour on exposure to the air. (A. Vogel.) The aqueous solution when boiled gives off acetic acid, and deposits brown cupric oxide. (Gay-Lussac, *Ann. Chim. Phys.* 37, 335.) According to Roux, the aqueous or alcoholic solution gives off acetic acid when boiled, and deposits a blue powder consisting of the terbasic salt, which becomes browner by continued boiling, and is probably converted into a mixture of cupric oxide with a small quantity of the terbasic salt. — The blue aqueous solution of the salt, mixed with aqueous sulphurous acid not in excess, assumes a green colour, and deposits yellow hydrate of cuprous oxide which redissolves in excess of sulphurous acid. The solution of the salt mixed with excess of sulphurous acid, forms an emerald-green mixture from which potash throws down yellow hydrate of cuprous oxide, and which when boiled (without potash), deposits a large portion of the copper in the form of brown-red cuprous oxide. (A. Vogel, *J. pr. Chem.* 29, 280.) — Drops of the dissolved salt placed upon bright iron, do not copper it at ordinary temperatures, or at most only at the edge; on the application of heat, however, more coppering takes place, but a temperature of 100° is required to make it sudden and complete. Small bars of iron completely immersed in the cold solution are often found uncoppered at the end of 24 hours; but if they are half drawn out, coppering takes place at the surface of contact between the air and the liquid, and extends thence through the entire mass. Steel bars completely immersed in the liquid remain constantly bright, but become coppered if they are half drawn out. Iron filings quickly decompose acetate of copper; but not after they have been freed from adhering air by trituration with water. Iron heated to a temperature much below redness, and still susceptible of being coppered in a solution of cupric sulphate or chloride, remains perfectly passive in a solution of the acetate. (Wetzlar, *Schw.* 50, 88.) — Various kinds of sugar reduce cuprous oxide or the metal from a solution of cupric acetate, especially with the aid of light or heat. (*vid.* Sugar.)

Crystals with 5 At. Water. — A solution saturated at 60°, of cupric acetate in water containing acetic acid, yields, when left in a cool place, transparent prisms, having the blue colour of common sulphate of copper. (Wöhler.) Short right rhombic prisms belonging to the right prismatic system, acuminated with the four *i*- and *y*-faces of the rectangular octohe-

drum resting on the lateral edges, and having the summit truncated by the p-face; cleavage parallel to u and u'; $u' : u = 115° 30'$; $i : u = 105° 30'$; $i : i$ above $p = 119° 54'$; $i : p = 150° 57'$. (G. Rose.) — The crystals heated to a temperature between 30° and 35°, become opaque, green, and moist, and are separated by slight pressure into small crystals of the ordinary salt, giving up at the same time 26·48 p. c. water, which may be pressed out between paper. This change is particularly remarkable when the crystals are immersed in warm water. The crystals contain 33·11 p. c. water, and are therefore $= C^4H^4CuO^4 + 5Aq$. (Wöhler, *Pogg.* 37, 166.)

The ordinary crystals dissolve in 17·4 pts. of cold water (Gehlen), in 5 pts. of boiling water, and in 14 pts. of boiling alcohol. (Wenzel.) Insoluble in ether. (Unverdorben, *Pogg.* 11, 53.) In water containing sugar they dissolve much less quickly than in pure water. (Holger, *Zeitschr. Phys. Math.* 3, 401.)

Respecting the compounds of acetic acid and copper, *viâ* Lassone (*Mém. de l'Acad.* 1773, 60; also *Crell. chem. J.* 4, 103). — Proust (*Ann. Chim.* 32, 26; also *Crell. Ann.* 1800, 1, 43; further: *J. Phys.* 47, 110; also *A. Gehl.* 6, 380). — Chenevix (*Gil.* 22, 170). — Gehlen (*Schw.* 4, 23). — R. Phillips (*Ann. Phil.* 23, 161; also *N. Tr.* 8, 1, 214; abstr. *Schw.* 36, 356). — Berzelius (*Pogg.* 2, 233).

Acetate of Cupric oxide and Ammonia. — Obtained by dissolving the monobasic acetate of cupric oxide in ammonia, and evaporating the solution at a gentle heat. Small blue crystals which smell of acetic acid and effloresce in warm air. (Coulon, *Ann. Chim.* 96. 327.)

Acetate of Cupric oxide and Lime. — *a.* Commercial verdigris contains blue crystals, whose optical properties differ from those of the simple monobasic acetate. (Brewster, *Schw.* 33, 342.)

Crystallized.			Ure.
CaO	28	11·39	11·4
2 CuO	80	32·52	32·0
$2\ C^4H^3O^3$	102	41·46	42·0
4 Aq	36	14·63	14·6
$C^4H^3CaO^4 + CuO,C^4H^3CuO^4 + 4Aq$	246	100·00	100·0

b. Obtained by heating a mixture of 1 At. crystallized verdigris and 1 At. hydrate of lime in an eight-fold quantity of water, and sufficient acetic acid to dissolve the precipitated cupric oxide, and evaporating the dark green filtrate to the crystallizing point at a temperature between 25° and 37°. — Large, transparent square prisms, or converted by truncation of the lateral edges into octagonal prisms, and resembling blue vitriol in colour. (*Comp.* Schabus. *Wien. Acad. Ber.* 1850, Juni, 59; *Jahresber.* 1850, 393.) Sp. gr. 1·4206. (Schabus.) They effloresce slightly in the air, fall to powder at 75°, giving off acetic acid at the same time, and dissolve readily in water. (Ettling, *Ann. Pharm.* 1, 296.)

Crystallized.			Ettling.
CaO	28	11·57	11·60
CuO	40	16·53	16·47
$2\ C^4H^3O^3$	102	42·15	43·88
8 Aq	72	29·75	30·63
$C^4H^3CaO^4,C^4H^3CuO^4 + 8Aq$	242	100·00	100·00

(Garot.) — When distilled, it does not melt, but gives off very strong acetic acid, having avery offensive odour like that of cat's urine, together with a small quantity of carbonic acid and carburetted hydrogen gas, and lastly mercury; the residue consists of very light charcoal (Garot); a small quantity of the salt sublimes undecomposed in white needles. (Stromeyer.) When boiled with water, it is resolved into 11 per cent. of metallic mercury which remains undissolved, and a solution of mercurous or mercuric acetate containing excess of acid. (Garot.) Dissolves in hot aqueous acetic acid with separation of mercury. (Stromeyer.) Boiling alcohol extracts all the acetic acid, and leaves all the mercurous oxide undissolved. (Garot.) Dissolves in 133 pts. of water at 12° or 15°, not in cold alcohol.

	Crystallized.		Dumas.	Garot.	Stromeyer.
Hg^2O	208	80·31	80·66	79·7	77·961
$C^4H^3O^3$	51	19·69	19·34	20·3	22·039
$C^4H^3Hg^2O^4$	259	100·00	100·00	100·0	100·000

Westendorf (*Dissert.* Gott. 1772, §§ 25 to 28), by strongly heating 1 pt. of mercuric oxide with 4 pts. of glacial acetic acid, obtained a sublimate like flowers of benzoin. Was this mercurous acetate?

Mercuric Acetate. — When red oxide of mercury is dissolved in cold acetic acid, and the filtrate abandoned to spontaneous evaporation, no crystals separate out (Proust, Garot), but a yellow deliquescent gum is obtained. (Dumas) (*Acid salt?*) But if the liquid be boiled with an addional quantity of the oxide till it is saturated (Garot; Stromeyer prefers gently heating it with strong acetic acid), the filtrate, on cooling, yields crystals of the mercuric salt. — If the filtrate be further evaporated without being left to cool, a reddish deposit of decomposed salt collects on the sides of the basin, and there remains a white mass which (by decomposition?) swells up like a sponge, is white and friable when cold, and does not deliquesce in the air but smells strongly of acetic acid. (Garot.) — When mercuric oxide, prepared, not in the dry way but by precipitating mercuric nitrate with soda, is boiled with acetic acid, a large quantity of mercurous acetate is formed and falls down as the liquid cools; but the remaining liquid, when carefully evaporated to a smaller bulk, yields crystals of the mercuric salt. (Garot.) — Concentrated solutions of mercuric nitrate and acetate of potash mixed together, deposit the mercuric salt in scales, which, however, are too soluble to be freed from nitric by washing with water. (Harff, *N. Br. Arch.* 5, 256.)

Rectangular tables and laminæ, resembling those of boracic acid, often truncated at the summits (Garot); sometimes transparent and with a glassy lustre, sometimes translucent and pearly (Stromeyer); duller than the mercurous salt; not flexible but friable; taste sharp and metallic; odour like that of acetic acid, disappearing when the salt is dry; reddens litmus; permanent in the air. (Garot). — The salt, when exposed to the air, gives off acid and is converted on the surface into a yellow basic salt. (Stromeyer.) Fuses when heated, giving off but a small quantity of acetic acid, then suddenly solidifies to a white granular mass, and afterwards decomposes rapidly, turning black, and giving off acetic acid containing an empyreumatic oil, also carbonic acid, and carburetted hydrogen gas, while mercury remains mixed with charcoal. (Stromeyer.) The aqueous solution undergoes no change when kept in stoppered bottles; when exposed to the air and heated, it gives off acetic acid, and deposits

yellow basic salt (red oxide, according to Garot); by continued is partly converted into mercurous acetate (Stromeyer); but when evaporated and cooled, likewise yields crystals of the salt. (Garot.) By boiling with sugar it is wholly converted mercurous salt. (A. Vogel.) The aqueous solution is imperfectly ed by ammonia, and yields a white precipitate, not however e acid is in excess (not in any case, according to Garot); the te contains mercuric oxide, ammonia, and acetic acid. In the rated state it is completely decomposed by potash or soda, yielding w precipitate, white however if ammonia has been previously if the solution be very dilute, no precipitate is formed. (Stro-) Aqueous protochloride of tin throws down all the mercury in tallic state; according to Garot, the two metals are thrown down er in the form of a black precipitate, so that the solution no longer ns any metal. (Garot.) Sulphuric acid throws down mineral turpe- (Harff.) Hydrosulphuric acid, in quantity not sufficient to produce lete decomposition, throws down a compound of sulphide of mercury mercuric acetate. (H. Rose, *Pogg.* 13, 69.) Common salt and nitrate lver give no precipitate. (Stromeyer, Garot.) The salt remains dry n exposed to the air. Dissolves in 4 pts. of water at 10° (Garot); in water at 19°, in about 1 pt. of boiling water (Stromeyer); dissolves 9° in 17·7 pts. of alcohol of sp. gr. 0·811, but with partial decompo- on and separation of a yellow basic salt. (Stromeyer.) Alcohol and er abstract acetic acid together with a trace of oxide from the crystals, l leave yellow mercuric oxide. (Garot.)

	Crystallized.			Stromeyer.	Garot.
HgO	108	67·92		67·664	67
$C^4H^3O^3$	51	32·08		32·336	33
$C^4H^3HgO^4$	159	100·00		100·000	100

On mercurous and mercuric acetates, *vid.* Wenzel (*von der Verwandschaft*, 206). ust (*A. Gehl.* 3, 33). Stromeyer (*Comment. Götting. recent.* 1). Garot (*J. Pharm.* 459; *N. Tr.* 14, 1, 179; abstr. *Mag. Pharm.* 16, 133). Dumas (*Bull. philom. Sc.* 1825, 7).

Acetate of Mercuric Oxide and Ammonia. — When mercurous acetate decomposed by ammonia not in excess, this compound separates in the m of a black powder, containing 85·9 p. c. mercurous oxide and 2·19 monia; it gives off acetic acid when treated with sulphuric acid, and monia when treated with potash, and dissolves in warm concentrated egar, leaving only a few globules of mercury. (Harff.)

Acetate of Mercuric Oxide and Ammonia. — Obtained by precipitating rcuric acetate with dilute ammonia (Stromeyer); or a mixture of rcuric acetate and acetate of ammonia with carbonate of soda. — hite powder, having a harsh metallic taste and containing 75·6 per cent. metal and 4·2 of ammonia. (Harff.)

A mixture of *acetate of mercury* [mercurous or mercuric ?] with acetate of baryta ot precipitated by ammonia. (Matteucci.)

Mercuric Cyanide with Mercuric Acetate. — Dilute acetic acid saturated th mercuric oxycyanide and evaporated, yields a white salt which ells of acetic acid, and when heated is resolved into cyanogen, acetic d, and mercury. (Johnston, *Phil. Trans.* 1839, 116.)

Mercuric Chloride with Cupric Acetate. — Cold saturated aqueous

effect also takes place in the preparation of the salt, if the solution does not contain a sufficient excess of acetic acid. — The salt dissolves readily in cold water. (Wertheim, *J. pr. Chem.* 29, 221.)

	Crystallized.		Wertheim.
AgO	116	20·17	20·06
$2\ U^2O^3$	288	50·09	49·71
$3\ C^4H^3O^3$	153	26·61	26·29
2 Aq	18	3·13	3·20
$C^4H^3AgO^4,2[C^4H^3(U^2O^2)O^4]+2Aq$	575	100·00	

Auric Acetate. — Concentrated acetic acid dissolves a small quantity of oxide of gold, when first brought in contact with it, but soon deposits the gold in the metallic state. (Pelletier.)

Platinous Acetate. — Formed by dissolving hydrated platinous oxide, while yet moist, in acetic acid. The greenish solution dries up to a dark greenish brown mass which redissolves in water, leaving only a small quantity of the oxide undissolved. (Berzelius, *Lehrb.*)

Acetic acid decomposes platinate of soda, taking up the soda with but little of the platinic oxide, and without acquiring a yellow tint. From the aqueous mixture of bichloride of platinum and acetate of soda, alcohol quickly reduces all the platinic oxide to platinum-black; hence platinic acetate appears to have been formed by double decomposition, for bichloride of platinum is not reduced by alcohol so quickly or so completely. (W. Döbereiner, *Pogg.* 28, 181.)

Rhodic Acetate. — Red solution. (Berzelius.)

Acetate of Rhodic Oxide and Soda. — Red salt, easily soluble in water, insoluble in alcohol. (Berzelius, *Lehrb.*)

Glacial acetic acid mixes very readily with *Ether*, but is separated from it by water. (Boullay.) — It mixes with *Alcohol*, producing a slight rise of temperature, and forming a liquid which is not solidified by any degree of cold. (Lowitz.)

Acetic acid forms soluble salts with the *Alkaloids.* — Glacial and concentrated acetic acid mix with a great number of *Volatile Oils*, and dissolve many *Camphors, Resins, Colouring Matters, Sugar, Gum, Protein-substances, &c.*

Schlippe (*J. pr. Chem.* 14, 383,) states that in wood-vinegar he observed, besides acetic acid, another acid resembling it but of peculiar nature, inasmuch as it yielded more soluble salts, and its soda-salt crystallized in a form differing from that of acetate of soda.

¶ Anhydrous Acetic Acid, $C^4H^3O^3$, or Acetic Acetate,

$$C^8H^6O^6 = \left.\begin{matrix} C^4H^3O^2 \\ C^4H^3O^2 \end{matrix}\right\} O^2.$$

Gerhardt. *Ann. Pharm.* 82, 127; 83, 112; *Compt. rend.* 34, 755, 902; *Chem. Soc. Qu. J.* 5, 127, 226. — Further and more fully: *N. Ann. Chim. Phys.* 37, 285.

Formation and Preparation.—1. By the action of chloride of benzoyl, $C^{14}H^5O^2Cl$, on fused acetate of potash. The first products of the action are chloride of potassium and acetate of benzoyl or benzoic acetate, $C^{18}H^8O^6$:

$$C^{14}H^5O^2,Cl + C^4H^3KO^4 = KCl + \left.\begin{matrix}C^{14}H^5O^2\\C^4H^3O^2\end{matrix}\right\}O^2.$$

This action takes place at the heat of the sand-bath. But if the acetate of potash be in excess, and the mixture be heated somewhat above the temperature at which the original substances act upon each other, a further action takes place and a colourless liquid distils over, which is anhydrous acetic acid, while anhydrous benzoic acid remains in the retort in combination with benzoate of potash. These new products are formed by double decomposition between 2 atoms of the benzoic acetate:

$$2\left(\left.\begin{matrix}C^{14}H^5O^2\\C^4H^3O^2\end{matrix}\right\}O^2\right) = \left.\begin{matrix}C^{14}H^5O^2\\C^{14}H^5O^2\end{matrix}\right\}O^2 + \left.\begin{matrix}C^4H^3O^2\\C^4H^3O^2\end{matrix}\right\}O^2$$

2. By the action of chloride of acetyl (or *othyl*) $C^4H^3O^2Cl$, on dry benzoate of soda. The reaction, which takes place without the aid of heat, is precisely similar to the preceding.—3. By the action of oxychloride of phosphorus, PO^2Cl^3, on acetate of potash. The acetate deprived of water by fusion is introduced into a tubulated retort, and the oxychloride of phosphorus admitted through the tubulus, drop by drop. A violent action takes place, the mixture becoming very hot without the application of heat from without; and a liquid distils over, which is the chloride of acetyl (or othyl), while terbasic phosphate of potash remains in the retort:

$$3C^4H^3KO^4 + PO^2Cl^3 = 3KO,PO^5 + 3(C^4H^3O^2,Cl).$$

If now this liquid be poured back again three or four times into the retort, so that it may remain for some time in contact with the acetate of potash, that salt being also in excess and pretty strongly heated, a further action takes place between the acetate of potash and the compound $C^4H^3O^2,Cl$, the result of which is the formation of anhydrous acetic acid: thus,

$$C^4H^3KO^4 + C^4H^3O^2,Cl = KCl + C^8H^6O^6.$$

The anhydrous acetic acid enters into combination with the acetate of potash, and a considerable degree of heat is required to destroy this compound and cause the anhydrous acid to distil over. The distillate is more or less contaminated with hydrated acetic acid and chloride of acetyl; but on redistilling the crude product, these impurities pass over at the commencement before the temperature rises to 137·5°, after which the pure anhydrous acid distils over. 40 pts. of fused acetate of potash, and 15 pts. crude oxychloride of phosphorus (obtained as a secondary product in the preparation of chloride of benzoyl (by the action of protochloride of phosphorus on benzoic acid) yield about 10 pts. of anhydrous acetic acid. This is the best mode of preparing the anhydrous acid when it is wanted in considerable quantities, but the first method yields the purest product.—4. By the action of terchloride of phosphorus on acetate of potash. When the liquid chloride is added drop by drop to the acetate of potash (about 1 pt. PCl^3 to more than 2 pts. of the acetate), the action begins without application of heat, and acetic chloride, amounting in quantity to about half the chloride of phosphorus used,

distils over mixed with a small quantity of chloride of phosphorus. On heating the residue after this action has ceased, anhydrous acetic acid distils over free from chloride, and in quantity equal to about a third of the chloride of phosphorus used. The product contains a small quantity of a phosphorus-compound, which causes it to impart a brownish colour to nitrate of silver; but it may be freed from this impurity by a second distillation with acetate of potash.

Properties. Colourless, very mobile, strongly refracting liquid, having a very powerful odour, similar to that of the hydrated acid, but stronger, and recalling at the same time that of the flowers of the white-thorn. Sp. gr. 1·073 at 20·5, which is nearly that of the hydrated acid, $C^4H^4O^4+Aq.$, at its greatest density. Boiling point 137·5° under a pressure of 750 mm. Vapour-density =3·47.

				Gerhardt.
4 C	24	47·05	46·87	46·89
3 H	3	5·88	5·95	5·87
3 O	24	47·07	47·18	47·24
$C^4H^3O^3$	51	100·00	100·00	100·00

	Vol.	Density.	Or:	Vol.	Density.
C-vapour	4	1·6640	C-vapour	8	3·3280
H-gas	3	0·2029	H-gas	6	0·4058
O-gas	1½	1·6639	O-gas	3	3·3278
Vapour	1	3·5308	Vapour	2	7·0616
				1	3·5308

Gerhardt and Williamson regard anhydrous acetic acid as water (H^2O), in which the 2 At. H are replaced by the radical C^2H^3O, called *Acetyl* by Gerhardt and *Othyl* by Williamson, so that its formula is $\left.\begin{matrix}C^2H^3O\\C^2H^3O\end{matrix}\right\}O$. (compare VII, 201.)

Decompositions. Fuming sulphuric acid becomes heated by contact with anhydrous acetic acid, carbonic acid being given off and a copulated acid produced, which forms a gummy salt with lead. — Potassium acts violently on anhydrous acetic acid, evolving a gas which does not take fire if the potassium be introduced by small portions at a time. The liquid, after a while, solidifies into a mass of needles consisting of a compound of anhydrous acetic acid with acetate of potash (*vid. inf.*) An oily substance is also produced having a very pleasant ethereal odour. — Finely divided zinc acts upon anhydrous acetic acid in a similar manner but less energetically, and only when heated in the water bath; hydrogen gas is then given off, and a soluble salt formed which is deposited in microscopic crystals on the surface of the metal, and greatly retards the action. On saturating the excess of acetic acid in the residue with carbonate of soda, the ethereal odour above mentioned is perceived. The hydrogen evolved, if collected immediately, has the same odour, burns with a bluish flame, and the product of the combustion renders lime-water turbid; but after passing through potash, it is inodorous, and when burnt yields nothing but pure vapour of water.

Combinations. Anhydrous acetic acid does not combine immediately *with Water*, but when poured into that liquid, falls to the bottom in oily

drops, which, if the mixture be heated or agitated for a while, ultimately dissolve. It absorbs water from damp air, and must therefore be kept in well-stoppered bottles.

According to the old theory of salts and acids, anhydrous acetic acid is supposed to exist, as such, in the hydrated acid and in all the acetates, *e. g.*, neutral acetate of potash $= KO,C^4H^3O^3$; ordinary biacetate of potash $= KO,HO,2C^4H^3O^3$ (*vid.* p. 290). Such a view of their constitution is however by no means necessary, and in fact the majority of chemists are now more inclined to adopt the views developed in the preceding pages; *e.g.* hydrated acetic acid $= C^4H^4O^4$; neutral acetate of potash $= C^4(H^3K)O^4$, &c., the ordinary biacetate $= C^4H^3KO^4 + C^4H^4O^4$; — or, according to Williamson & Gerhardt, the hydrated acid $= \left.\begin{matrix}C^4H^3O^2\\H\end{matrix}\right\}O^2$, [or $\left.\begin{matrix}C^2H^3O\\H\end{matrix}\right\}O$]; neutral acetate of potash $= \left.\begin{matrix}C^4H^3O^2\\K\end{matrix}\right\}O^2$, &c. There appears however to be a class of acetates which really contain the anhydrous acid combined with a neutral acetate. Gerhardt has in fact obtained a potash-salt of this nature, viz.:

Anhydrous Biacetate of Potash. — $C^4H^3KO^4,C^4H^3O^3$. Formed by the action of potassium on anhydrous acetic acid (p. 336); also by dissolving fused acetate of potash in anhydrous acetic acid at a boiling heat. — In either case, the salt separates on cooling in colourless needles very soluble in water, but less deliquescent than the ordinary neutral acetate. When purified by pressure from excess of anhydrous acetic acid, and then dried over sulphuric acid, it remains unaltered in the air for a few hours, provided the air is not very damp. When this salt and the ordinary neutral acetate are placed side by side, the latter liquefies almost immediately, while the biacetate remains dry for a much longer time; nevertheless it gradually becomes moist. When heated in the dry state, it gives off anhydrous acetic acid and leaves perfectly pure neutral acetate of potash.

			Gerhardt.
8 C	48·0	32·17	
6 H	6·0	4·02	
K	39·2	26·27	26·10
7 O	56·0	37·54	
$C^4H^3KO^4,C^4H^3O^3$	149·2	100·00	

The composition of this salt may also be expressed by the formula, $KO,2C^4H^3O^3$; it is analogous to bichromate of potash, $CrKO^4,CrO^3$, or $KO,2CrO^3$. Gerhardt's formula (equiv. VII, 17) is $2C^2H^3KO^2,C^4H^6O^3$. Similar salts are formed by other anhydrous organic acids, *e. g.* benzoic (*q. v.*) ¶.

Sulphide of Ethyl, or Sulphethyl. $C^4H^5S = C^4H^4,HS$.

DÖBEREINER. *Schw.* 61, 377.
REGNAULT. *Ann. Chim. Phys.* 71, 387; also *Ann. Pharm.* 34, 24; also *J. pr. Chem.* 10, 264.

Hydrosulphuric Ether, Ethylic Sulphide, Schwefeläthyl, Aethylsulfür, Schwefelvinafer, Ether hydrosulfurique, Sulfure d'Ethyle. — First observed by Döbereiner in 1831; more exactly investigated in 1839, by Regnault.

Preparation. 1. An alcoholic solution of potash is divided into two equal parts, the first saturated completely with hydrosulphuric acid, and then mixed with the other, so that the solution may contain monosulphide of potassium. The potash may be in excess, but not the hydrosulphuric acid. The liquid is introduced into a tubulated retort, and vapour of hydrochloric ether — evolved by boiling alcohol with hydrochloric acid and purified by passing first through water, then through oil of vitriol, then through water again — is passed into it through the tubulus. As soon as the alcoholic liquid is completely saturated with the hydrochloric ether, it is heated by a few coals till it distils, the vapour of hydrochloric ether being still passed through it. After a short time, a large quantity of chloride of potassium separates out, whilst hydrosulphuric ether distils over, mixed with alcohol. If the residue in the retort be now left to cool, again saturated with vapour of hydrochloric ether, and the process conducted as before, an additional quantity of sulphide of ethyl distils over:

$$C^4H^5Cl + KS = C^4H^5S + KCl.$$

On adding water to the distillate, the hydrosulphuric ether rises to the top in a separate layer; it must then be repeatedly shaken up with water, afterwards decanted and rectified over chloride of calcium. (Regnault.)

2. A mixture of equal parts of the strongest hydrochloric acid and alcohol of sp. gr. 0·81, set aside for 24 hours in contact with tersulphide of antimony or protosulphide of iron, and then distilled, yields a distillate, which, when the hydrosulphuric acid has evaporated, has a pungent odour like that of *Asafœtida*, and a taste like that of radishes; when mixed with water, it becomes turbid, and yields oily drops, which have the same odour, are lighter than water, and when burnt, emit an odour of sulphurous acid; the residue smells like phosphorus and radishes. (Döbereiner.)

3. Dry sulphide of potassium distilled with dry sulphovinate of baryta, yields a product having the same properties. (Lowig.)

Properties. Colourless liquid of sp. gr. 0·825 at 20°; boils at 73°. Vapour-density = 3·10. Has a pungent odour like that of garlic, but not nearly so unpleasant as that of mercaptan. (Regnault.)

				Regnault.		Vol.	Density.
4 C	24	53·33	53·84	C-vapour	4		1·6640
5 H	5	11·11	11·11	H-gas	5		0·3465
S	16	35·56		S-vapour	½		1·1093
C^4H^5S	45	100·00		C^4H^5S-vapour	1		3·1198

Ether in which the oxygen is replaced by sulphur.

Decompositions. Hydrosulphuric ether takes fire when poured into chlorine gas; but if dry chlorine be slowly passed into it in daylight, the liquid then exposed to sunshine, chlorine again passed into it while exposed to diffused daylight, then the action of the sun's rays repeated, &c., quadrichlorinated hydrosulphuric ether, C^4Cl^4HS, is formed, and hydrochloric acid evolved. (Regnault.) This formation of C^4Cl^4HS is probably preceded by that of C^4ClH^4S, of $C^4Cl^2H^3S$, and of $C^4Cl^3H^2S$. (Regnault.) ¶ When chlorine is passed into hydrosulphuric ether, even in a place where there is but very little light, and without access of air, the liquid becomes heated and often takes fire (whence it *is not* safe to operate on large quantities); chloride of ethyl is then

and introduced into a tubulated retort; the liquid is then poured upon it, and the mixture distilled at a gentle heat into a receiver surrounded with ice. As soon as the greater part of the mercaptan has distilled over, the receiver should be changed, because at the latter part of the operation more water goes over, and the mass is very apt to froth over; the distillation may then be continued as long as oily drops of mercaptan distil over with the water. A large quantity of mercaptan remains dissolved in the water, but cannot be separated from it. The *crude* mercaptan thus obtained and mechanically separated from the water, still contains sulphuretted hydrogen and a peculiar *indifferent* oil; that is to say, an oil which does not act upon acetate of lead. It is converted into *purified mercaptan*, by agitating it with an equal quantity of water twice renewed; placing it in contact with chloride of calcium; rectifying it by a heat gradually rising to 112°; agitating the distillate with finely powdered mercaptide of mercury, till a decanted sample exhibits no trace of sulphuretted hydrogen when tested with sugar of lead (and acts but very slightly or not at all on nitrate of lead, and forms with very dilute acetate of lead, not a brownish but a pure lemon-yellow precipitate); and rectifying it again, till it boils constantly at 60°. — The following mode of obtaining purified mercaptan is more circuitous, and attended with greater loss. The crude mercaptan is shaken up with an equal bulk of water, and the treatment repeated till a sample behaves with lead-salts in the manner above mentioned, — a mode of purification which requires a large quantity of water, and is therefore attended with great loss, in consequence of the mercaptan dissolving in the water. The mercaptan is then distilled at a heat gradually rising to 120°, till the residue is reduced to $\frac{1}{10}$ of the original quantity, and consists chiefly of the above-mentioned indifferent oil with a small quantity of bisulphide of ethyl; this partial rectification is repeated till the distillate (amounting to $\frac{2}{3}$ of the whole) boils at 62°, after which it is placed in contact with chloride of calcium, and rectified once more. The crude mercaptan may also be first freed from the indifferent oil by fractional rectification, and then from sulphuretted hydrogen by careful addition of mercuric oxide.

Purified mercaptan has a sp. gr. of 0·845 at 17°. If it be made to combine with mercuric oxide, alcohol still extracts from the mass a quantity of the indifferent oil; the latter also separates when the purified mercaptan is combined with potash and dissolved in water. To convert the purified mercaptan into *pure mercaptan*, it must then still be freed from this residual portion of the indifferent oil. For this purpose, 1 pt. of mercuric oxide is introduced into a tubulated retort surrounded with a freezing mixture; 3 or 4 pts. of purified mercaptan gradually poured through the tubulus by means of an S-tube, whereupon great heat is produced, especially at first, but a certain quantity of the mercuric oxide remains unaltered at the bottom; the ice is then removed, and the retort gradually heated to 140°, to melt the mercaptide of mercury; the mixture agitated till the rest of the mercuric oxide disappears and the bottom of the retort is entirely covered with black sulphide of mercury; and then heated in a bath of aqueous chloride of calcium, till scarcely anything passes over at 114°. The first portions of the distillate consist of mercaptan, which must be several times poured back; afterwards nothing but water passes over. The fused mercaptide of mercury in the retort is then decanted from the sulphide of mercury into a basin; triturated, when solid, with 95 p. c. alcohol to the consistence of a thin paste;

washed on a filter with alcohol, till the liquid which runs through no longer becomes milky on being mixed with water (in consequence of the separation of indifferent oil), but merely exhibits a slight turbidity, due to the presence of shining particles of mercaptide of mercury. A small portion of the mercaptide of mercury is taken up by the alcohol, especially at the beginning, through the medium of the indifferent oil, but it may be recovered by distilling off the alcohol. — The mass, after being washed with alcohol, is dried in the air; kept for some time in the fused state at a temperature somewhat above 100° to drive off all the alcohol; finely pounded when cold, with addition of quartz-powder to divide the particles of the compound, which, being unctuous, would otherwise adhere together; the powder introduced into a long, wide, glass tube, bent downwards at the right extremity, and immersed in water of 50°, contained in a leaden trough; sulphuretted hydrogen gas, previously washed with water and dried by chloride of calcium, passed through the tube from left to right; and the vapour of mercaptan thereby set free, passed from the right bent extremity into a knee-tube, the descending part of which reaches to the middle of a long-necked flask, surrounded with ice and salt. The excess of sulphuretted hydrogen is conducted from the flask through a long gas-delivery tube into a bell-jar containing potash and standing in mercury. The mercaptide of mercury becomes heated when decomposed by sulphuretted hydrogen; but its temperature must be kept below 85°, to prevent it from melting; towards the end of the operation, the water is heated to 62°, and the sulphuretted hydrogen passed through less quickly. The receiver is changed occasionally, for the purpose of ascertaining when the decomposition is at an end. — Lastly, to remove the sulphuretted hydrogen from the distillate, it must be frequently agitated with small quantities of mercaptide of mercury, till the mercaptan no longer changes the colour of that compound, or imparts a brownish tint to an alcoholic solution of acetate of lead. The mercaptan must then be freed from water by agitation with chloride of calcium, and finally distilled. (Zeise.)

2. Since the protosulphide of barium obtained by igniting sulphate of baryta with charcoal, is somewhat contaminated with bisulphide, the mercaptan prepared by Zeise's process always contains a certain quantity of bisulphide of ethyl. A purer product may be obtained by completely saturating one measure of potash-ley of sp. gr. 1·28 — 1·30 with hydrosulphuric acid, mixing it with one measure of an aqueous solution of sulphovinate of lime of the same density, and distilling at 100°. The mixture swells up slightly; evolves a small quantity of hydrosulphuric acid at the beginning of the distillation; and gives off all the mercaptan, together with water, so that nothing more is obtained by heating the mixture more strongly over the open fire. The mercaptan, which is obtained in large quantities, is freed from hydrosulphuric acid by distillation in contact with mercaptide of mercury, and from water by contact with chloride of calcium. (Liebig.)

3. Alcoholic potash completely saturated with hydrosulphuric acid gas, and then treated in a tubulated retort with hydrochloric ether, just as in the preparation of hydrosulphuric ether (p. 338), yields perfectly pure mercaptan, free from bisulphide of ethyl and all other impurities. (Regnault, *Ann. Chim. Phys.* 71, 390.)

Properties. Transparent and colourless liquid, which may be cooled to —22° without solidifying. (Zeise.) A drop placed upon a glass rod and

exposed to a gentle current of air, solidifies to a buttery, foliated mass, which melts and evaporates in the course of a few seconds, (Liebig.) Sp. gr. = 0·842 at 15° (Zeise), 0·835 (Liebig). Appears not to refract light strongly (Zeise); boils at 61° to 63°, under a pressure of 28′ (Zeise); with platinum-foil immersed in it, it boils, either alone or under water, constantly at 36·2° under a pressure of 27″ 8‴ (Liebig). Vapour-density 2·188 (Regnault). Perfectly neutral to vegetable colours, even in the state of solution. Has an ethereal taste and odour, with a very powerful tinge of garlic. (Zeise.)

			Zeise.	Liebig.
4 C	24	38·71	39·05	39·26
6 H	6	9·68	9·56	9·63
2 S	32	51·61	51·39	51·11
$C^4H^6S^2$	62	100·00	100·00	100·00

	Vol.	Density.
C-vapour	4	1·6640
H-gas	6	0·4158
S-vapour	½	2·2186
Mercaptan-vapour	2	4·2984
	1	2·1992

Alcohol in which the oxygen is replaced by sulphur. According to Zeise, it is $H,C^4H^5S^2$, *i. e.*, hydrogen combined with the hypothetical radical *Mercaptum*. According to Liebig and Regnault, it is C^4H^5S,HS, *i. e.*, a compound of hydrosulphuric acid with sulphide of ethyl, (*comp.* Persoz, *Chim. molecul.* 863.) — It is remarkable that mercaptan has a lower boiling point than sulphide of ethyl, though the contrary holds good with alcohol and ether. — ¶ According to the views entertained by Williamson, Gerhardt, and Chancel, respecting similar compounds, the rational formula of mercaptan will be $\left.\begin{matrix}C^2H^5\\H\end{matrix}\right\}S$ and it may be regarded as derived from sulphuretted hydrogen $\left.\begin{matrix}H\\H\end{matrix}\right\}S$, by the substitution of 1 At. ethyl C^2H^5 for 1 At. H, just as alcohol is derived from water. ¶.

Decomposition. 1. Mercaptan may be set on fire in the air by a burning body held at a considerable distance, and burns with a blue sulphurous flame. (Zeise.) — 2. Moderately strong nitric acid imparts to mercaptan a blood-red colour, due to the formation of a compound of mercaptan with nitric oxide. On distilling the mixture, a watery distillate passes over, on which this same blood-red liquid floats; and at the bottom of the liquid which remains in the retort, sulphite of sulphethyl, $C^4H^5S^2O^2$, collects in the form of a colourless oil;

$$C^4H^6S^2 + 3O = C^4H^5S^2O^2 + HO.$$

Strong nitric acid acts more violently, producing scarcely anything but bisulphethylic acid, $C^4H^5S^2O^4$ (hyposulphethylic acid, $C^4H^5S^2O^5$, according to later investigations). Scarcely a trace of free sulphuric acid is formed, unless the nitric acid be very highly concentrated. (Löwig and Weidmann, *Pogg.* 49, 323.) — At a few degrees below 0°, nitric acid of sp. gr. 1·23 does not act upon mercaptan, but at a gentle heat it acts violently, giving off nitrous acid, and imparting a blood-red colour to the liquid, which gradually deposits the oily compound $C^4H^5S^2O^2$. (H. Kopp, *Ann. Pharm.* 35, 343.) — 3. Mercaptan is decomposed by contact with

many heavy metallic oxides, even when they are dissolved in acids, the action being often attended with great evolution of heat, and the products being a metallic mercaptide and water; with several metallic chlorides also it forms a mercaptide of the metal and hydrochloric acid. (Zeise):

$$C^4H^6S^2 + HgO = C^4H^5HgS^2 + HO;$$

and

$$C^4H^6S^2 + HgCl = C^4H^5HgS^2 = HCl.$$

4. Potassium decomposes mercaptan, giving off hydrogen and forming mercaptide of potassium. (Zeise.)

Combinations. Mercaptan is but sparingly soluble in *Water*, to which nevertheless it imparts its taste and smell; 7 drops of mercaptan require 25 grm. water to dissolve them. (Zeise.)

Mercaptan dissolves *Phosphorus* and *Sulphur* slowly, but in considerable quantity. (Zeise.)

It dissolves a large quantity of *Iodine.* The dark brown solution mixed with a comparatively small quantity of water, yields a brown oil which floats on the watery liquid; but a larger quantity of water shaken up with the mercaptan, produces complete decoloration. (Zeise.)

Mercaptan absorbs a large quantity of *Nitric oxide gas*, acquiring thereby a dark brown colour. The mixture, when exposed to the air, evolves nitrous fumes and gives up its nitric oxide, especially in sunshine. (Löwig & Weidmann. *Pogg.* 49, 323.)

Metallic Mercaptides. — For the formation of these compounds, vid. *Decompositions of Mercaptan*, 3 and 4. According to the substitution-theory, they may be regarded as mercaptan in which 1 At. hydrogen is replaced by 1 At. metal, $= C^4H^5MS^2 = C^4H^4,HMS^2$; and, according to the radical-theory, either as compounds of mercaptum with a metal $= M,C^4H^5S^2$ (Zeise); or as sulphur-salts, C^4H^5S,MS, in which sulphide of ethyl forms the base and the metallic sulphide [even sulphide of potassium!] the sulphur-acid, these compounds being in fact more intimate, as the acid character of the metallic sulphide is more decided. — The mercaptides of the heavy metals are insoluble in water, but some of them dissolve in alcohol.

Mercaptide of Potassium. — Potassium becomes strongly heated by contact with mercaptan, pure hydrogen being given off with strong effervescence, and a white granular body formed. An excess of mercaptan must be used, and afterwards expelled by heat. — The compound may be heated in a glass tube considerably above 100° without decomposing; but at a stronger heat, it turns black, melts, gives off vapour, and leaves a residue from which water extracts sulphide of potassium, leaving charcoal undissolved. Mercaptide of potassium is decomposed with violent effervescence by sulphuric and hydrochloric acid, even when dilute. It dissolves quickly and abundantly in water, forming a strongly alkaline solution which gives a yellow precipitate with lead-salts, even after gentle heating, but a white precipitate after being more strongly heated. The solution decomposes when exposed to the air, forming carbonate of potash. Alcohol dissolves less of this compound than water. The alcoholic solution forms a pure yellow precipitate with lead-salts, even after boiling; but when exposed to the air in a watch-glass, it deposits small crystals whose aqueous solution forms a white precipitate

with lead-salts, and brick-red with silver-salts. — The potassium-compound is not formed when mercaptan is mixed with potash; it is true that hydrate of potash becomes softened by long contact with mercaptan; but on adding water, potash and mercaptan are obtained in the free state. A mixture of mercaptan and alcoholic potash left to itself for several days and then treated with water, yields free mercaptan and aqueous alcoholic potash, still containing a small quantity of mercaptan which may be expelled by gentle heating.

Mercaptide of Sodium. — Formed like the potassium-compound, but with less violent action; dissolves also readily in water, forming a strongly alkaline liquid.

Aqueous mercaptide of potassium does not precipitate *Chloride of Calcium*; with *Chloride of Barium* it forms a few flakes, which, however, seem to be nothing but carbonate of potash.

Aqueous mercaptide of potassium forms with sulphate of *Zinc* a copious snow-white precipitate; mercaptan itself does not precipitate zinc-salts. (Zeise.)

Mercaptide of Lead. — Formed by precipitating an alcoholic solution of neutral acetate of lead with alcoholic mercaptan. If the solutions are very dilute, the precipitate is white and small in quantity. The precipitate formed in alcoholic solutions is crystalline, but less so as the mercaptan is more free from bisulphide of ethyl, which appears to hold the precipitate in solution for a while. Nitrate of lead is not precipitated by mercaptan, but forms a precipitate with mercaptide of potassium; pure protoxide of lead immersed in mercaptan, swells up to a yellow mass, which turns black even after washing with alcohol, and burns like tinder when set on fire; carbonate of lead acts upon mercaptan in a similar manner but less quickly. — Lemon-yellow, crystalline powder, or shining needles and laminæ which soon resolve themselves into a felt-like mass. When slightly heated, it fuses and turns black. Dissolves in excess of an alcoholic solution of acetate of lead. Caustic potash does not seem to act upon it. (Zeise.)

Alcoholic mercaptan does not precipitate alcoholic *Sesquichloride of Iron*; aqueous mercaptan imparts a reddish colour to ferric sulphate, and then forms a white precipitate.

Mercaptide of Copper. — Finely pulverized cupric oxide placed in contact with pure mercaptan in a close vessel, swells up with it in the course of 24 hours, forming an almost colourless magma, which dries up to a yellowish white mass. This mass sustains a tolerably strong heat without decomposition; burns in the flame of a candle, with a bluish-green light; is not decomposed by boiling potash; forms a colourless solution with moderately strong hydrochloric acid; and dissolves sparingly in alcohol. — This compound may also be obtained by precipitating a cupric salt with aqueous mercaptide of potassium, which forms a yellowish precipitate if the copper-salt is in excess, — or by precipitating alcoholic acetate of copper with alcoholic mercaptan, which produces a white gelatinous precipitate. (Zeise.) — When vapour of mercaptan is passed over very hot but not red-hot cupric oxide, water is given off and a white saline mass formed. (Liebig.)

Mercaptide of Mercury. — When mercaptan, either in the pure state, or dissolved in water or alcohol, is brought in contact with mercuric

oxide, great heat is evolved (sufficient, when pure mercaptan is used, to produce slight detonation), and water and mercaptide of mercury are formed. With corrosive sublimate it forms the same compound together with hydrochloric acid; hence alcoholic mercaptan likewise forms a white precipitate with an aqueous solution of mercuric nitrate or corrosive sublimate. But mercurous nitrate forms with aqueous mercaptan a black precipitate (the colour arising from metallic mercury); and calomel when digested for some time with mercaptan, forms hydrochloric acid and turns nearly black. (Zeise.) — The compound is best obtained by placing the mercaptan in a tubulated retort surrounded with a freezing mixture, adding the mercuric oxide in small portions and in somewhat less than the equivalent quantity, then heating the compound till it melts, and drawing off the excess of mercaptan together with the water. (Zeise.) — The compound may be purified by solution in boiling alcohol and crystallization. (Liebig.)

Mercaptide of mercury, when solidified after fusion, is colourless, of crystalline texture, greasy and soft to the touch, and somewhat tough when triturated. From its solution in mercaptan containing bisulphide of ethyl, or in alcohol, it crystallizes in small colourless crystals having a strong silky lustre. Melts between 85° and 87°, forming a liquid which resembles a fixed oil, and solidifies slowly on cooling. Even in the fused state it is almost inodorous, but when triturated it emits a faint odour, different from that of mercaptan. It is not altered by air or by light. (Zeise.)

Crystallized.			*Zeise.*
4 C	24	14·91	14·73
5 H	5	3·10	3·01
Hg	100	62·11	62·40
2 S	32	19·88	19·67
$C^4H^5HgS^2$	161	100·00	99·81

Decompositions. 1. Mercaptide of mercury when heated above its melting point becomes first yellowish, then greyish and opaque, and emits a suffocating vapour which attacks the eyes strongly, and deposits metallic mercury. At 130° the mass, which has now become greyish black, gives off a nearly colourless oil, which is heavier than water, neutral, rich in sulphur, difficult to set on fire, and when dissolved in alcohol does not precipitate acetate of lead; hence it is probably bisulphide of ethyl. When heated above 175°, it still yields a trace of oil together with a sulphurous mass, and leaves a mixture of mercury and carbonaceous matter, which, when more strongly heated, yields metallic mercury and a kind of cinnabar (which, probably from containing carbon, does not assume a fine red colour), so that after strong ignition continued for some time, nearly the whole is sublimed. No gas is evolved. — 2. Mercaptide of mercury may be set on fire with tolerable facility in the flame of a candle. — 3. Strong nitric acid acts violently on this compound, forming a red-brown solution which becomes colourless when heated, and after continued exposure to heat, yields an oil on addition of water. Aqua-regia acts in a similar manner, excepting that it evolves a suffocating vapour, smelling strongly of chloride of sulphur. — 4. Concentrated hydrochloric acid heated for some time with mercaptide of mercury dissolves it completely, forming a liquid which becomes very milky when mixed with potash. Dilute hydrochloric acid digested for some time with mercaptide of mercury, forms a liquid which when cooled or mixed with potash, deposits crystals having a very

strong lustre. Oil of vitriol and concentrated phosphoric acid act but slightly on this compound. — 5. Hydrosulphuric acid decomposes mercaptide of mercury, both in the moist and in the dry way, yielding mercaptan and black sulphide of mercury. — 6. Aqueous protosulphide of potassium digested with it, separates first black and then red sulphide of mercury; with a certain proportion, however, a colourless alkaline solution is formed, containing mercaptide of potassium and a small quantity of mercaptide of mercury, yielding a white precipitate when boiled or evaporated, a grey precipitate with sulphide of potassium, and yellow with lead-salts. — 7. Lead decomposes mercaptide of mercury in a state of fusion, forming mercaptide of mercury and lead-amalgam. — 8. Mercaptide of mercury fuses readily with corrosive sublimate, and when more strongly heated, yields a colourless ethereal liquid, which smells both of mercaptan and of bisulphide of ethyl, and leaves a dark brown residue capable of being drawn out into threads, and containing metallic mercury. — It is not decomposed by boiling with water or with aqueous potash, unless the potash-solution be boiled down to that temperature at which the mercaptide of mercury would decompose if alone; in that case mercury is separated. (Zeise.)

Mercaptide of mercury dissolves very sparingly in alcohol; and the solution, when mixed with water, becomes turbid from separation of crystalline particles; alcohol containing bisulphide of ethyl dissolves it more readily. (Zeise.) It dissolves in 12....15 pts. of boiling 80 p. c. alcohol, and separates therefrom in considerable quantity on cooling, in the form of soft colourless laminæ which have a silvery lustre when dry. (Liebig.)

Mercaptide of Silver. — Mercaptan acts upon oxide of silver much in the same manner as upon oxide of gold. The aqueous solution of mercaptan forms with aqueous nitrate of silver, a copious snow-white precipitate, which however appears always to contain nitric acid. Pure mercaptan acts but very slightly on chloride of silver at ordinary temperatures; the alcoholic solution acts more quickly. (Zeise.)

Mercaptide of Gold. — Formation. Mercaptan, even when mixed with a fourfold to sixfold quantity of alcohol, acts rapidly on teroxide of gold, producing a very intense heat, and sometimes even fire; in the latter case the product is not white but black. — Mercaptan converts terchloride of gold into white mercaptide of gold, the action being attended with violent evolution of hydrochloric acid gas; alcoholic mercaptan throws down the same compound from an aqueous solution of terchloride of gold. [Since the white compound which forms is not $Au,3C^4H^5S^2$, but $Au,C^4H^5S^2$, it follows that in its formation from teroxide or terchloride of gold, according to the equation:

$$C^4H^6S^2 + AuO^3 = C^4H^5AuS^2 + HO + 2O,$$

2 At. oxygen or chlorine are set free and act upon another portion of the mercaptan; hence perhaps the very great evolution of heat which takes place in the formation of mercaptide of gold from the oxide.] — If mercaptan be precipitated from a very dilute alcoholic solution by excess of terchloride of gold, the filtrate neutralized with lime, and then distilled, pure alcohol passes over, and the strongly acid chloride of calcium which remains, becomes turbid when mixed with water, and smells of heavy hydrochloric ether; hence the 2 At. chlorine from the terchloride

of gold, which do not take hydrogen from the mercaptan, appear to exert a decomposing action on the alcohol. (Zeise.)

The mercaptide of gold obtained by precipitating alcoholic terchloride of gold with mercaptan is brownish at first; but if the mixture contains excess of mercaptan and a sufficient quantity of alcohol, it soon becomes tolerably white when shaken up. Gold is completely precipitated by mercaptan, even from very dilute solutions. If the liquid be decanted from the mercaptide of gold, and mixed with an excess of the alcoholic solution of the terchloride, a more pulverulent pale grey precipitate is formed, which becomes greenish grey after drying. The liquid filtered from this precipitate forms with water a copious white precipitate, which becomes pale yellow when dry, decomposes at a much lower temperature than the mercaptide of gold, assuming a brownish yellow and afterwards a black-brown colour, and yielding a red-brown distillate which has the odour of chloride of sulphur. This precipitate is perhaps a compound of gold with a chlorinated decomposition-product of mercaptan. — When aqueous or alcoholic mercaptide of potassium is mixed with a quantity of terchloride of gold not sufficient for complete precipitation, a brownish yellow precipitate of mercaptide of gold is formed, which soon turns white, and the liquid emits a peculiar odour; if the chloride of gold is in excess, the precipitate contains chlorine. (Zeise.)

Preparation. A solution of 1 pt. hydrochlorate of auric chloride (perfectly dried in vacuo over hydrate of potash) in 15 to 20 pts. alcohol is gradually added to a solution of 1 pt. of partially purified or pure mercaptan in 60 to 70 pts. of alcohol of sp. gr. 0·816, so that the mercaptan may be in excess; more alcohol is added to the thin gummy mixture, after half an hour; the precipitate left to subside; the liquid decanted; the precipitate washed, first with cold then with warm alcohol, whereby it is completely freed from chlorine, provided the chloride of gold was not in excess during the mixing; and, lastly, dried over hydrate of potash in vacuo. (Zeise.)

Properties. White; pasty when moist, hard when dry, like hydrate of alumina; dull, amorphous, not greasy to the touch; inodorous even when rubbed; not altered by air or light. (Zeise.)

Dried in vacuo at ordinary temperatures.			Zeise.
4 C	24	9·23	9·44
5 H	5	1·92	1·93
Au	199	76·54	76·34
2 S	32	12·31	12·36
$C^4H^5AuS^2$	260	100·00	100·07

Mercaptide of gold undergoes no change at 190°; at 225° and upwards it turns brownish, and yields, without fusion or evolution of gas, a very pale yellow distillate; and at a temperature below redness, leaves a residue of nearly pure gold. Sometimes a trace of sulphur also sublimes, and gold remains together with a trace of carbon. — The *distillate* is a neutral oil of about 1·000 sp. gr.; it smells rather of mercaptan than of bisulphide of ethyl, although its alcoholic solution, when treated with lead, mercury, or silver salts, exhibits but traces of mercaptan (no sulphuretted hydrogen). Potassium evolves from the distillate but a small quantity of gas, and only on first coming in contact with it, and forms a white saline mass (which appears to contain a trace of mercaptide of potassium and becomes brownish when heated, as also does the supernatant mass, both being

afterwards found to contain small quantities of sulphide of potassium); if the distillate be treated with potassium in the cold and the product dissolved in alcohol, a slightly alkaline solution is obtained, which does not precipitate either lead or mercury salts. This distillate is probably a mixture of various decomposition-products, together with a trace of mercaptan, but does not appear to contain mercaptum, $C^4H^5S^2$, which perhaps cannot exist in the free state. (Zeise.)

Mercaptide of Platinum. — Formed by precipitating alcoholic mercaptan with a quantity of alcoholic bichloride of platinum not sufficient for complete precipitation, washing the copious, light yellow, muddy precipitate with alcohol, and drying. (Zeise.)

Light yellow and loosely coherent after drying.

				Zeise.
4 C	24	....	15·00	
5 H	5	....	3·12	
Pt	99	....	61·88	..... 61·87
2 S	32	....	20·00	
$C^4H^5PtS^2$	160	....	100·00	

This compound sustains a heat nearly approaching to redness before it turns black; by dry distillation, it yields a thin liquid which is more volatile than that obtained from mercaptide of gold, and has likewise a different odour. The residue subjected to a stronger heat, glows and remains black; if afterwards ignited in contact with the air, it gives off sulphurous acid and leaves platinum; it is therefore sulphide of platinum. (Zeise.)

Mercaptan dissolves sparingly in weak *Alcohol*, mixes in all proportions with strong alcohol, and requires large quantities of water to separate it from the solution; but it then separates in considerable quantity. — With *Ether* it likewise mixes in all proportions. (Zeise.)

Zeise's Indifferent Sulphuretted Oil.

Zeise obtained, on several occasions, a peculiar oil which he sometimes distinguishes by the epithet *indifferent*, and which differs from protosulphide of ethyl, from mercaptan, and from bisulphide of ethyl.

This oil is formed in small quantity in the preparation of mercaptan from sulphide of hydrogen and barium and a sulphovinate, and consequently the mercaptan requires to be purified from it. In the preparation of bisulphide of ethyl from bisulphide of barium and a sulphovinate, small quantities of this indifferent oil likewise pass over with the bisulphide of ethyl. It is however obtained in greatest abundance, mixed with about $\frac{1}{11}$ mercaptan, by distilling 1 At. protosulphide of barium with a concentrated solution of 1 At. sulphovinate of baryta. The mixture becomes turbid at 60°, then gummy and covered with scum; at the end of the distillation nothing remains but sulphate of baryta, If too much water be added, the whole of the oil remains dissolved in the watery distillate. The oily mixture of this indifferent oil and mercaptan, which passes over with the watery distillate (which is free from alcohol), begins to boil at 70°, but the boiling point gradually rises to 102°; by repeated fractional distillation, it may be separated into a more volatile portion, the mercaptan, and a less volatile portion, the indifferent oil. The latter

may be freed from the last portions of mercaptan by agitation with water and oxide of lead, and from water by rectification over chloride of calcium.

This compound is a transparent and colourless oil, which has a density of 0·8449 at 18°. It has an odour of garlic not however resembling bisulphide of ethyl, but mercaptan, weaker however and less ethereal. It is neutral. Burns with a redder flame than mercaptan, producing a larger quantity of sulphurous acid. Dissolves in water more readily than mercaptan; its alcoholic solution produces no turbidity in lead or mercury salts. Contains 22·26 per cent. of carbon, 10·82 hydrogen, 27·99 sulphur, 38·93 oxygen; its formula is therefore approximately = $C^4H^{12}S^2O^6$ = Mercaptan + 6 Aq. (Zeise.)

¶ Acetyl-mercaptan. $C^4H^4S^2 = C^4H^3S,HS$.

WEIDENBUSCH. *Ann. Pharm.* 66, 152; abstr. *Pharm. Centr.* 1848, 852; *J. pr. Chem.* 46, 252; *Chem. Gm.* 1849, 34; *Laur. & Gerh. Compt. rend.* 1849, 28; *Jahresber.* 1847—8, 550.

Formed from the oily compound $C^{12}H^{13}S^7$ (p. 279), by abstraction of 1 At. HS:

$$C^{12}H^{13}S^7 - HS = 3C^4H^4S^2.$$

A drop of strong sulphuric acid added to the oil, causes it instantly to solidify into a white crystalline mass consisting of the new compound, while sulphuretted hydrogen escapes. A larger quantity of sulphuric acid dissolves the crystals, producing a transient brown colour; but they are reprecipitated on the addition of water. The same crystalline mass is obtained on passing hydrochloric acid gas through the oil. — A few bubbles of chlorine passed into the oil produce the same effect; but a larger quantity of chlorine decomposes the new compound, producing an oily liquid of intolerable odour, and doubtless containing chlorine and sulphur. — Acetyl-mercaptan is also formed by heating the compound $C^{12}H^{13}S^7$, by placing it over oil of vitriol under a bell-jar, and by exposing its saturated aqueous solution to the air.

Dazzling white, lustrous needles having an unpleasant allinceous odour; they begin to sublime at 45,° and then assume the form of snow-white, loosely coherent masses. They dissolve in alcohol and ether, sparingly also in water, and distil over with the latter, floating on the surface of the distillate. From its alcoholic solution, the compound crystallizes on the sides of the vessel in beautiful dendrites.

				Weidenbusch.	
4 C	24	40·00	39·44	39·64	
4 H	4	6·67	7·10	6·87	
2 S	32	53·33	53·05	53·40	
$C^4H^4S^2$	60	100·00	99·59	99·91	

May be regarded as C^4H^3S,HS, analogous to common mercaptan C^4H^5S,HS; or as aldehyde in which the oxygen is replaced by sulphur.

Acetyl-mercaptan is perfectly neutral and is not effected by ammo- or potash. With nitric acid it froths up strongly, decomposes, and

probably yields a copulated sulphur-acid analogous to that which mercaptan forms under similar circumstances (p. 343).

Silver-compound. $2(AgO,NO^5)+3C^4H^4S^2$. When an alcoholic solution of acetyl-mercaptan is mixed with an alcoholic solution of nitrate of silver, a tolerably thick white precipitate is formed which does not change colour; on heating it, sulphide of silver separates and a silver-compound remains dissolved. The solution filtered at a boiling heat, yields on cooling, nacreous spangles whose composition agrees with the above formula.

				Weidenbusch.	
12 C	72	13·84		13·49	13·52
12 H	12	2·31		2·45	2·77
6 S	96	18·46		18·26	18·53
2 AgO	232	44·63		44·77	44·59
2 NO^5	108	20·76		20·88	20·86
$2(Ago,NO^5)+3C^4H^4S^2$	520	100·00		99·85	100·27

The crystals have the odour of acetyl-mercaptan, which compound is separated from them by alkalis; they assume a darker colour when exposed to light; blacken and give off nitrous acid when heated; — the aqueous solution decomposes when evaporated, yielding sulphide of silver. ¶

Bisulphide of Ethyl. $C^4H^5S^2$.

ZEISE. *Pogg.* 31, 371.
PYR. MORIN. *Bibl. univ.* 1839, Nov. 150; also *Pogg.* 48, 483; also *J. pr. Chem.* 19, 417.
LÖWIG. *Pogg.* 27, 550. — LÖWIG & WEIDMANN. *Pogg.* 49, 326.
CAHOURS. *N. Ann. Chim. Phys.* 18, 263; also *Ann. Pharm.* 61, 98.

Zweifach-Schwefelathyl, Thialöl, Bisulphure d'Ethyle. — First discovered by Zeise.

Formation. — 1. When an alkaline sulphovinate is brought in contact with a polysulphide of potassium (Zeise):

$$C^4H^5KO^2,2SO^3 + KS^2 = C^4H^5S^2 + 2(KO,SO^3).$$

If the sulphide of potassium contains more than 2 At. sulphur, the excess is precipitated. Zeise also prepared bisulphide of ethyl by mixing sulphovinate of wine-oil with alcoholic or aqueous polysulphide of potassium; in the former case, a large quantity of sulphate of potash was precipitated, and the bisulphide of ethyl remained dissolved in the alcohol; in the latter, it fell to the bottom of the aqueous solution of sulphate of potash. It is a question whether the product in this case was not a mixture of bisulphide of ethyl and an oil of wine altered by the action of sulphuretted hydrogen.

2. In the decomposition of aqueous [bi-]sulphide of potassium by oxalic ether. (Löwig.)

$$2C^4H^5O,C^4O^6 + 2KS^2 = 2C^4H^5S^2 + C^4K^2O^8.$$

3. In the decomposition of sulphite of sulphethyl by caustic potash. (Löwig & Weidmann.)

Preparation. — 1. A mixture of 2 pts. pentasulphide of potassium and 3 pts. sulphovinate of potash is distilled in a retort with 5 pts. water; more water added when the residue becomes thick; the distillation continued; and this treatment repeated three or four times as long as oil continues to pass over. If a larger proportion of pentasulphide of potassium be used, the oil obtained is very impure.—The yellow and still impure bisulphide of ethyl is separated from the water which has passed over with it; shaken up several times with large quantities of fresh water; and dried for several days over chloride of calcium. Of this oil, which is contaminated with a more fixed oil (hence its boiling-point rises from 150° to 200°) a quantity is distilled off sufficient to raise the boiling-point to 190°; the distillate again distilled till the boiling-point rises to 180°; and this treatment repeated till a distillate is obtained, which passes over at 151° without leaving any residue. The quantity of the pure product thus obtained is about half that of the impure oil. (Morin.) — ¶ 2. Muspratt (*Chem. Soc. Qu. J.* 3, 19) distils together in a large retort, equal portions of the concentrated solutions of sulphovinate of lime and tersulphide of potassium; washes the oily product repeatedly with distilled water; and then rectifies it several times over chloride of calcium. ¶

By triturating sulphide of potassium (obtained by igniting sulphate of potash with charcoal) with oxalic ether to a thick paste, distilling at a slowly increasing heat, and frequently returning the distillate into the retort, Löwig obtained a distillate, which, after being freed from oxalic ether by continued agitation with strong potash or sulphide of barium, and rectified over chloride of calcium, exhibited the following characters: Transparent and colourless liquid, lighter than water, and having a disgusting odour like that of *Asafœtida*, so strong that a drop of the liquid is sufficient to fill a large room with the odour; it has a persistently sweet taste, and is neutral to vegetable colours. Burns with a blue flame, forming sulphurous acid. It is not decomposed by boiling with aqueous potash, but on distilling it with pulverized hydrate of potash, a small portion is resolved into sulphide of potassium and alcohol; with alcoholic potash, it gives a precipitate resembling mercaptide of potassium. With an alcoholic solution of neutral acetate of lead it forms a yellow precipitate, but has no action on mercuric oxide. With potassium, at a moderate heat, it gives off only a few bubbles. Dissolves sparingly in water, imparting to it its own taste and odour, and mixes in all proportions with alcohol and ether. — This liquid was pronounced by Löwig (*Pogg.* 37, 550) to be sulphide of ethyl, C^4H^5S; but he afterwards found by analysis (*Chem. d. org. Verbind.* Aufl. 1, 1, 464), that it is $C^4H^5S^2$. It differs, however, from Morin's $C^4H^5S^2$ in density, taste, behaviour with mercuric oxide, &c.

Properties. Sp. gr. about equal to that of water, so that it first floats upon water, and then, perhaps from absorbing water, sinks to the bottom. Boils at 151°, passing over undecomposed. Neutral to vegetable colours. Has a very strong and repulsive alliaceous odour (according to Muspratt, it has a most disgusting smell when crude, but after rectification the smell is only slightly alliaceous); when inhaled it is very apt to produce headache; tastes first sharp and afterwards sweetish; 10 drops of it given to a rabbit cause convulsive movements, from which however the animal slowly recovers. Vapour-density =4·270. (Cahours.)

			Morin.	Löwig & Weidmann.
4 C	24	39·34	39·38	39·18
5 H	5	8·20	8·26	8·46
2 S	32	52·46	52·65	52·83
$C^4H^5S^2$	61	100·00	100·29	100·47

	Vol.	Density.
C-vapour	4	1·6640
H-gas	5	0·3465
S-vapour	½	2·2186
Vapour of $C^4H^5S^2$	1	4·2291

The bisulphide of ethyl analyzed by Löwig & Weidmann was obtained by the action of potash on sulphite of sulphethyl. — The formula of this compound does not accord with the nucleus-theory, unless it be doubled, — an alteration which is justified to a certain extent by the vapour-density.

Decomposition. 1. Bisulphide of ethyl burns with a blue flame, producing sulphurous acid. (Morin.) — 2. It is rapidly decomposed by chlorine, especially in sunshine. (Cahours.) — 3. With bromine, it evolves heat and forms a mixture which is perfectly soluble in water, and yields by distillation a liquid having the pungent odour of hydrobromic acid, and at the same time somewhat aromatic. (Morin.) — 4. Fuming nitric acid at a boiling heat acts violently upon it, and forms a colourless liquid which no longer smells like garlic, except when saturated with potash; it precipitates chloride of barium, but yields a much smaller quantity of sulphate of baryta than it would if all the sulphur were converted into sulphuric acid. (Morin.) Moderately strong sulphuric acid acts violently upon the oil, forming, besides sulphuric acid, a copulated acid [hyposulphethylic acid, $C^4H^6S^2O^6$, according to Muspratt], which with potash, baryta, and oxide of lead, forms salts which are soluble in water and crystallizable. (Cahours.) — 5. Oil of vitriol heated with bisulphide of ethyl decomposes it, with evolution of sulphurous acid. (Morin.) — 6. Strong potash-ley decomposes it at a boiling heat and with access of air, forming a milky-liquid. (Morin.) — 7. Bisulphide of ethyl acts slowly on mercuric oxide, forming a yellow mass; its alcoholic solution forms white flakes with corrosive sublimate, and yellowish white flakes with acetate of lead. (Morin.)

Bisulphide of ethyl dissolves very sparingly in *water* and aqueous *sulphurous acid*, and not at all in cold oil of vitriol, but mixes in all proportions with *alcohol* and *ether*, the latter of which liquids separates it completely from water. (Morin.)

According to Cahours (*N. Ann. Chim. Phys.* 18, 264) there exists also a *Tersulphide of Ethyl*=$C^4H^5S^3$; for on distilling pentasulphide of potassium with sulphovinate of lime, though a distillate is obtained containing abundance of bisulphide of ethyl, yet on rectifying this liquid, bisulphide of ethyl passes over first, and afterwards yellowish $C^4H^5S^3$, which is but very slightly volatile, and behaves with chlorine and nitric acid like the bisulphide.

When oxalic ether dissolved in alcohol is mixed with an alcoholic solution of pentasulphide of potassium, and water added to the mixture, a white, fusible, sweetish substance is precipitated, which burns with a blue flame and a smell of sulphur, and dissolves readily in alcohol, — perhaps *Pentasulphide of Ethyl*, $C^4H^5S^5$. (Löwig, *Chem. d. org. Verb.* Aufl. 1, 1, 464.)

Bisulphide of Ethylene. C^4H^4,S^2.

LÖWIG & WEIDMANN (1840). *Pogg.* 49, 123; also *J. pr. Chem.* 19,

Zweifach-Schwefelvine, [*Fevine*], — called *Einfach-Schwefelätherin* by L and Weidmann, who assign to it the formula C^2H^2S, although the compound be not to the methylene but to the ethylene series.

A mixture of alcoholic protosulphide of potassium and Dutch li $C^4H^4Cl^2$, exposed to the air (p. 381), deposits this compound in the of a white powder, which must be washed on a filter and dried.

Snow-white, very loosely coherent powder. Sometimes it is yello and bakes together when heated.

When subjected to dry distillation, it yields products similar to t obtained from the following compound, $C^4H^4S^4$.

				Löwig & Weidmann.	
4 C	24	40·00	39·25	36·18
4 H	4	6·67	6·60	6·07
2 S	32	53·33	53·04	58·16
C^4H^4,S^2	60	100·00	98·89	100·41

Tetrasulphide of Ethylene. $C^4H^4S^4$.

LÖWIG & WEIDMANN (1839). *Pogg.* 46, 84. — *Pogg.* 49, 128; also *J. Chem.* 19, 432.

Vierfach-Schwefvine, [*Fovine*]. — Called *Zweifach-Schwefelätherin* by Löw Weidmann.

The alcoholic solution of the sulphide of potassium obtained igniting [bi ?]sulphate of potash with charcoal, when mixed with Du liquid and set aside in a close vessel, deposits gradually, and in 14 completely, a white powder which must be washed with water and dri

Yellowish, very soft powder, which melts somewhat below 100° has a sweetish taste.

			Löwig & Weidmann.
4 C	24	26·09	26·13
4 H	4	4·35	4·74
4 S	64	69·56	69·87
$C^4H^4S^4$	92	100·00	100·74

[Acetic acid in which the oxygen is replaced by sulphur].

This compound, when subjected to dry distillation, boils up, giv off combustible gases and a yellowish liquid containing sulphur, leaves a spongy charcoal also containing sulphur. Burns in the air w a blue flame, forming sulphurous acid. — In dry chlorine gas it assu a greenish colour at first, and afterwards fuses, with formation of hy

Selenide of Ethyl, or Selenethyl. $C^4H^5Se = C^4H^4,HSe$.

LÖWIG. *Pogg.* 37, 552;—further, *Chem. d. org. Verb.* Aufl. 2, 2, 432.
JOY. *Ann. Pharm.* 86, 35.

Hydroselenic ether, Selenäthyl, Selenvinafer, Selenwasserstoffäther.

Finely pounded selenide of potassium mixed to the consistence of a thick paste with pure oxalic ether, then gently heated in a retort for some hours, and afterwards distilled, yields a liquid which smells and tastes like sulphide of ethyl, and when set on fire, burns, with an odour of radishes and deposits selenium. (Löwig.) — According to Löwig, (*Chem. d. organ. Verbind.*) the same compound is obtained by distilling selenide of potassium with aqueous sulphovinate of lime.

¶. Selenethyl is a clear, pale-yellow liquid, having a most insufferable odour; it is much heavier than water, and does not mix with it. When set on fire, it burns continuously, with evolution of red vapours of selenium.

Calculation.

4 C	24	34·78
5 H	5	7·24
Se	40	57·98
C^4H^5Se	69	100·00

Iodide of Selenethyl, C^4H^5 Se I. — Produced when a solution of the nitrate or chloride is mixed with hydriodic acid. Black liquid having a semi-metallic lustre, sinking in water, very much like bromine. It is inodorous and does not solidify at 0°. (Joy.)

Bromide of Selenethyl. — Separates in the form of a lemon-yellow oil, heavier than water, when a solution of the nitrate is mixed with hydrobromic acid. (Joy.)

These two compounds dissolve readily in ammonia, and form an oxybromide and oxyiodide of selenethyl, which however have not been further examined.

Chloride of Selenethyl. C^4H^5SeCl. — The solution of selenide of ethyl in nitric acid behaves with hydrochloric acid just like that of tellurethyl (p. 386); on the addition of the acid it becomes milk-white, and immediately afterwards drops of an oily body separate out.

The substance is the chloride of selenethyl. It is a transparent light yellow liquid which sinks in water; when quite pure, it appears to be inodorous. It is somewhat soluble in water and still more in hydrochloric acid, which circumstance renders some care necessary in preparing it.

			Joy.
4 C	24·0	22·99	
5 H	5·0	4·79	
Se	40·0	38·31	
Cl	35·4	33·91	33·87
C^4H^5SeCl	104·4	100·00	

The greater part of the chloride of selenethyl obtained as above having been left for a considerable time in contact with the liquid containing hydrochloric and nitric acid, in which it had been produced, a number of transparent and colourless crystals were observed to form at the separating surface of the two liquids. These crystals were very well defined, and, considering the small quantity, of considerable magnitude. This body, from its mode of decomposition when heated, and its ultimate analysis, appears to be an organic compound containing chlorine and selenium. It does not exhibit the characters of a hydrate of the chloride of selenethyl when treated with water, or by any other means. It dissolves readily in water and in alcohol, and separates out unchanged on evaporating the liquids. Its aqueous solution is not clouded by hydrochloric acid; it has an acid reaction. The body appears to be an acid; for it forms with ammonia, a highly crystalline mass, from which the ammonia is eliminated by potash. Hydrochloric acid did not precipitate chloride of selenethyl from it, a proof that no oxychloride of selenethyl had been formed by the action of the ammonia. On the other hand, sulphurous acid added to it, separated selenethyl. Analysis showed that it contains 13·68 per cent. carbon, 4·298 hydrogen, and 20·05 chlorine; whence we may infer that it contains 4 eq. chlorine to 4 eq. carbon. (Joy).

Oxychloride of Selenethyl. $C^4H^5SeO + C^4H^5SeCl$.—Chloride of selenethyl dissolves readily in ammonia, producing chloride of ammonium and oxychloride of selenethyl. After evaporating the solution, the oxychloride may be extracted by absolute alcohol. It crystallizes in highly-lustrous colourless cubes, generally grouped in stellate masses. Hydrochloric acid added to its aqueous solution throws down the oily chloride of selenethyl; and sulphurous acid throws down a stinking mixture of selenethyl and the chloride. (Joy.)

Nitrate of Selenethyl.—Formed by dissolving selenethyl in hot moderately-strong nitric acid, the action being attended with evolution of nitric oxide gas. It was not obtained in the dry state, but only in the form of a concentrated solution, which began to decompose when further evaporated. (Joy.) ¶

In the preparation of selenium-mercaptan (*vid. inf.*), as the heat increases after that compound has passed over, a second distillate is obtained, which appears to be a mixture of protoselenide and biselenide of ethyl (C^4H^5Se and $C^4H^5Se^2$) or of selenium-mercaptan and biselenide of ethyl. It is yellow, heavier than water, has an extremely repulsive odour, burns like selenium-mercaptan, does not act on mercury, and contains 63·73 p.c. of selenium. (Siemens, *Ann. Pharm.* 61, 360.)

Selenium-mercaptan. $C^4H^6S^2 = C^4H^4,H^2S^2$.

Wöhler & Siemens (1846). *Ann. Pharm.* 61, 360.

Obtained by saturating aqueous potash with hydroselenic acid gas in an apparatus filled with hydrogen, and distilling the resulting solution of selenide of hydrogen and potassium with concentrated sulphovinate of

lime, the air being as much as possible excluded. Hydroselenic acid gas is first given off, and afterwards water passes over together with a heavy, yellow, intolerably stinking liquid. This liquid, after being separated from the watery distillate, is placed in contact with chloride of calcium and distilled into a fresh receiver, whereupon selenium-mercaptan passes over first, and afterwards selenide of ethyl. (*vid. sup.*)

Selenium-mercaptan is a thin, transparent, colourless liquid, heavier than water, boiling considerably above 100°, and having an extremely repulsive odour, resembling that of the cacodyl-compounds.

It burns with a deep bright blue flame, giving off thick white and red vapours of selenious acid and selenium. The vapour passed through a tube heated to low redness is decomposed with separation of selenium.— A mixture of selenium-mercaptan and chlorate of potash takes fire and explodes on the addition of hydrochloric acid. Selenium-mercaptan appears not to be completely oxidized by chlorine or nitric acid. — When passed in the state of vapour over red-hot copper wire, it is completely decomposed, forming crystalline selenide of copper, emitting an odour like that of benzole, and depositing a small quantity of charcoal. In this reaction, the copper takes up 68·05 pts. of selenium from 100 pts. of selenium-mercaptan.

Selenium-mercaptan is insoluble in water. In contact with mercuric oxide it becomes heated, makes a hissing noise, and forms a yellow, easily fusible substance, which dissolves in hot alcohol, and separates from it in an amorphous condition on cooling. The alcoholic solution of selenium-mercaptan also forms a thick yellow precipitate with corrosive sublimate. (Wöhler & Siemens.)

			Wöhler & Siemens.
4 C	24	21·82	
6 H	6	5·45	
2 Se	80	72·73	68·05
$C^4H^6S^2$	110	100·00	

The specimen of selenium-mercaptan analyzed was probably contaminated with hydroselenic ether, and consequently yielded too little selenium. (Wöhler & Siemens.)

Iodide of Ethyl. C^4H^4,HI.

GAY-LUSSAC. *Ann. Chim.* 91, 89; also *Schw.* 13, 449 and 14, 63; also *Gilb.* 49, 259.

SERULLAS. *Ann. Chim. Phys.* 25, 323; also *Mag. Pharm.* 9, 148.— *Ann. Chim. Phys.* 42, 119; also *J. Pharm.* 15, 444.

EMILE KOPP. *N. J. Pharm.* 6, 109; also *Comp. rend.* 18, 871; also *J. pr. Chem.* 33, 182.

RICH. MARCHAND. *J. pr. Chem.* 33, 186.

FRANKLAND. vid. Memoirs cited on page 168.

Hydriodic Ether, Hydriodnaphtha, Iodwasserstoffäther, Iodäthyl, Iodvinefe, Éther hydriodique, Iodure d'Éthyle. — Discovered by Gay-Lussac in 1815.

Preparation. 1. By distilling 2 vol. absolute alcohol with 1 vol. hydriodous acid of sp. gr. 1·7. The distillate is transparent, colourless and has no acid reaction; on the addition of water, it deposits the hydriodic ether, which may be purified by washing with water. (Gay-Lussac.) — 2. A mixture of 1 pt. phosphorus and 8 pts. iodine is intro-

duced into a tubulated retort containing 22·5 pts. alcohol of 37° Bm.; sufficient iodine added to dissolve the iodide of phosphorus completely; the mixture distilled as long as any spirituous liquid passes over; and the hydriodic ether separated from the distillate by cold water. The residue in the retort mixed with 7·5 pts. alcohol and distilled again, yields an additional quantity of hydriodic ether. (Serullas.) Or better: 16 pts. of iodine are dissolved in 40 pts. alcohol of 38° Bm. and 1 pt. phosphorus added in small pieces, while the liquid is continually shaken; nearly the whole is then distilled over, the residue mixed with 10 pts. more of alcohol, and the distillation repeated. (Serullas.)

3. Iodine is dissolved in 85 per cent. alcohol; phosphorus added till the solution becomes decolorized; then more iodine, the vessel being constantly kept cool from without; then again phosphorus till the colour disappears, — this alternation being repeated till non-spontaneously inflammable phosphuretted hydrogen begins to escape. The liquid, when distilled, yields nearly as much hydriodic ether as the calculation requires. The residue is a strongly acid fluid mixture of phosphoric, phosphovinic, and a small quantity of hydriodic acid, with red oxide of phosphorus floating in it. (E. Kopp.)

4. Fifty grammes of iodine and between 200 and 300 grammes of absolute alcohol are shaken together in a flask of the capacity of half a litre; a stick of phosphorus held within a spiral of platinum wire fixed into the air-tight cork, is then introduced into the liquid; the mixture, as soon as it becomes colourless, shaken up to dissolve the rest of the iodine; fresh portions of iodine continually introduced and the liquid decolorized by the phosphorus &c., — the phosphorus then removed; the decolorized liquid distilled to $\frac{1}{5}$; and the hydriodic ether separated from the alcohol by water. This mode of operating prevents the solid iodine from coming in contact with the phosphorus, whereby much heat is evolved, and a red-brown mass produced, consisting of oxide and iodide of phosphorus. In this process, 252 pts. (2 At.) iodine consume 63·5 pts. (2 At.) phosphorus, and yield only 146 pts. (nearly 1 At.) iodide of ethyl. The residue in the retort consists of phosphovinic acid, a small quantity of hydriodic acid, and an organic acid containing iodine. If the phosphorus be not removed before the distillation, or rather, as soon as the liquid has become colourless, the hydriodic ether will contain phosphorus, whereby its boiling point will be raised to 73°; but it may be freed from phosphorus by distilling it with a small quantity of iodine, and from excess of iodine by shaking it up with mercury till it becomes colourless, and distilling again. It may be completely dehydrated by leaving it for some time in contact with chloride of calcium, and then distilling. (R. Marchand.)

¶ 5. Frankland pours 35 pts. of absolute alcohol on 7 pts. of phosphorus in a vessel surrounded with ice-cold water; then adds gradually 23 pts. of iodine; decants the liquid from the undissolved portion, and distils it in the water-bath; washes the distillate, and mixes it with iodine till it exhibits a faint colour; then dries it over chloride of calcium; and rectifies it repeatedly over a mixture of chloride of calcium, mercury, and oxide of lead. ¶

According to E. Kopp, the equation for the formation of hydriodic ether by iodine and phosphorus is:

$$5C^4H^6O^2 + 5I + P = 5C^4H^5I + 5HO + PO^5;$$

but according to Marchand:

$$5C^4H^6O^2 + 10I + 2P = 5C^4H^5I + 5HI + 2PO^5.$$

In either case, the phosphoric acid unites with another portion of the alcohol to form phosphovinic acid; and, according to Marchand, the hydriodic acid likewise forms an organic acid containing iodine.

Properties. Transparent and colourless liquid; sp. gr. = 1·9206 at 23·3°; [according to Frankland, it is 1·9464 at 16°; according to Pierre, 1·9755 at 0°]. Boils at 64·6°. [In Frankland's preparation, the thermometer with its bulb in the vapour showed a temperature of 71·6°, but rose to 72·2° with its bulb in the liquid, the barometer being at 746·5mm.; according to Pierre, it boils at 70° when the barometer stands at 751·7mm.]. Vapour-density = 5·4749 [5·417, according to Marchand]. Has no acid reaction; its odour is strong and peculiar. (Gay-Lussac.)

				Marchand.		Vol.	Density.
4 C	24	15·48		15·31	C-vapour	4	1·6640
5 H	5	3·23		3·28	H.gas	5	0·3465
I	126	81·29			I-vapour	1	8·7336
C^4H^5I	155	100·00			C^4H^5I-vapour	2	10·7461
						1	5·3730

Decompositions. ¶ 1. Iodide of ethyl, when exposed to *light*, turns brown from separation of iodine, the action taking place slowly in diffused daylight, quickly in direct sunshine. Even in the latter case however, the decomposition is arrested when the brown colour has attained a certain degree of intensity; but if the free iodine be removed by agitation with mercury, the action again goes on. It may be rendered continuous by introducing a small quantity of iodide of ethyl into a glass flask filled with mercury and inverted in a basin of the same metal, and exposing the arrangement to the sun's rays, — or better, by placing it in the focus of an imperfectly polished concave mirror (if the mirror were perfectly polished, the heat would be too great). The iodine then unites with the mercury, and a quantity of gas is set free. To obtain a sufficient quantity for examination, it is best to use several flasks. This decomposition is purely an effect of light, not of heat; for iodide of ethyl is not decomposed by mercury, even at 150°. Moreover, the decomposition goes on rapidly, if the vessel containing the mercury and iodide of ethyl be surrounded with water or even with a solution of chloride of copper, which absorbs nearly all the heat-rays but transmits nearly all the luminous rays; but if the vessel be surrounded with a solution of bichromate of potash, which transmits heat but stops the luminous rays, decomposition does not take place. The gas evolved in this action, after being left for 12 hours over a dilute solution of sulphide of potassium (to absorb vapour of undecomposed iodide of ethyl and prevent access of oxygen), is found to contain in 100 measures: 14·34 vol. olefiant gas, 17·90 hydride of ethyl, C^4H^6, and 67·76 ethyl. The direct action of the solar light is simply to liberate the ethyl, and form iodide of mercury:

$$C^4H^5I + Hg = C^4H^5 + HgI;$$

but a small portion of the ethyl is resolved into olefiant gas and hydride of ethyl:

$$2C^4H^5 = C^4H^4 + C^4H^5,H.$$

In presence of water, the action goes on in the same manner, and the gas obtained is composed of olefiant gas, ethyl, and hydride of ethyl in the same proportions. This decomposition of iodide of ethyl by sunshine

might serve as a means of measuring the intensity of the solar rays. (Frankland, *Chem. Soc. Qu. J.* 3, 322.) ¶

2. Iodide of ethyl passed in the state of vapour through a *red-hot tube* yields very brown hydriodous acid, a combustible gas containing carbon, a small quantity of charcoal, and a non-combustible substance containing iodine, which collects in the tube in the form of a waxy deposit, melting below 100, and insoluble in water, alkalis and acids. (Gay-Lussac.) The vapour passed through a narrow glass tube at a dull red heat, yields a gaseous mixture of 2 vol. olefiant gas to 1 vol. hydrogen, and a brown-red crystalline body, $C^4H^4I^2$, contaminated with free iodine. (E. Kopp.) According to the equation:

$$2C^4H^5I = C^4H^4I^2 + C^4H^4 + 2H.$$

the olefiant gas and the hydrogen should be obtained in equal volumes.—3. Iodide of ethyl thrown on *red-hot coals*, emits violet vapours but does not take fire. (Gay-Lussac.) 4. When exposed to the *air*, it assumes a rose-colour in the course of a few days, from separation of iodine. (Gay-Lussac.)—5. Dry *Chlorine gas* passed through iodide of ethyl at ordinary temperatures, suddenly throws down iodine, with evolution of chloride of ethyl. (Dumas & Stas, *Ann. Chim. Phys.* 73, 152; also *Ann. Pharm.* 35, 162; also *J. pr. Chem.* 21, 374):

$$C^4H^5I + Cl = C^4H^5Cl + I.$$

By continued action of the chlorine, the separated iodine is converted into chloride of iodine. (Marchand.)—6. *Nitric acid* likewise causes an immediate separation of iodine.—7. *Oil of vitriol* quickly turns it brown.—8. Vapour of iodide of ethyl passed over hot *potash-lime*, yields pure olefiant gas. (Dumas & Stas):

$$C^4H^5I + KO = C^4H^4 + KI + HO.$$

Aqueous potash does not decompose iodide of ethyl immediately. Potassium may be kept in it without alteration. (Gay-Lussac.)

¶ 9. Iodide of ethyl is decomposed by various metals under the influence of light or heat, the iodine uniting with a portion of the metal, while the ethyl is partly set free, and partly enters into combination with another portion of the metal, forming a compound metallic radical. Thus: (*a*) *Zinc* heated in a sealed tube with iodide of ethyl forms iodide of zinc, ethyl, and *zinc-ethyl*, C^4H^5Zn. On breaking off the extremity of the tube under water, the whole of the ethyl and part of the zinc-ethyl escape in the form of gas; the latter is decomposed by the water, yielding oxide of zinc and hydride of ethyl, and a portion of the former splits up spontaneously into olefiant gas and hydride of ethyl; hence the gas obtained is a mixture of ethyl, hydride of ethyl, and olefiant gas (*compare* pp. 159, 160; also VII, 171).—(*b*) Similarly, when iodide of ethyl is enclosed in a sealed tube together with *Tin* (in the shape of thin strips of tinfoil), and either heated to 180°, or exposed to the rays of the sun concentrated by a parabolic reflector, part of the iodide of ethyl is decomposed, yielding ethyl and iodide of tin, while the rest combines with the metal, forming iodide of *stanethyl*, C^4H^5SnI. This compound collects on the sides of the tube in straw-coloured needles; and on opening the tube under water, a gaseous mixture is evolved, consisting of olefiant gas and hydride of ethyl produced in the manner above described. (Frankland, *Ann. Pharm.* 85, 329; *Chem. Soc. Qu. J.* 6, 57.) Similar results have been obtained by Cahours and Riche. (*Compt. rend.*

35, 91.) — (*c*) Iodide of ethyl heated with a mixture of *stannide of potassium* or *stannide of sodium* and quartz-sand (to moderate the action) yields a mixture of stanethyl with various other compound radicals containing tin and ethyl, viz.

Methylene-stanethyl	$Sn^2(C^4H^5)^2$	analogous to	Methylene....	C^2H^2
Elayl-stanethyl ..... or Ethylene-stanethyl....	$Sn^4(C^4H^5)^4$	,,	Ethylene	C^4H^4
Aceto-stanethyl	$Sn^4(C^4H^4)^3$	,,	Acetyl	C^4H^3
Metho-stanethyl.....	$Sn^2(C^4H^5)^3$	,,	Methyl	C^4H^3
Etho-stanethyl	$Sn^4(C^4H^5)^5$	,,	Ethyl.....	C^4H^5

The proportions in which these several compounds are formed vary according to the relative quantities of the iodide of ethyl and of the alloy, the composition of the alloy itself, and the quantity of quartz-sand added. (Löwig, *Mittheil. d. naturforsch. Gesellsch. in Zürich*, Oct. 1852; *J. pr. Chem.* 75, 385; abstr. *Chem. Gaz.* 1853, 101, 126, 149, 170; *Jahresber.* 1852, 577.) [For details respecting these compounds, see vol. VIII.] — (*d*) According to some preliminary experiments made by Frankland, most of the metals are capable of decomposing iodide of ethyl under the influence of heat or light, and entering into combination with the ethyl; among those which appear to promise the most interesting results are: arsenic, antimony, chromium, iron, manganese, and cadmium. — *Mercury* does not appear to be capable of uniting with ethyl; for when iodide of ethyl is exposed to sunshine in contact with mercury, nothing is obtained but iodide of mercury, and a mixture of ethyl, hydride of ethyl, and olefiant gas (p. 360). — 10. Iodide of ethyl heated with zinc-ethyl in a sealed tube yields ethyl and iodide of zinc:

$$C^4H^5Zn + C^4H^5I = ZnI + (C^4H^5)^2.$$

By heating iodide of ethyl with zinc-methyl or zinc-amyl, or zinc-ethyl with iodide of ethyl or amyl, it is probable that a compound metallic radical, ethylo-methyl or ethylo-amyl, would be obtained. (Brodie, *Chem. Soc. Qu. J.* 3, 405; compare VII, 174.) ¶

Combinations. Iodide of ethyl dissolves very sparingly in water, readily in alcohol. (Gay-Lussac.)

Biniodide of Ethylene. C^4H^4,I^2.

FARADAY. *Ann. Phil.* 18, 118; abstr. *Schw.* 31, 488; abstr. *Pogg.* 5, 325. — *Quart. J. of Sc.* 13, 429; also *Schw.* 36, 237.
REGNAULT. *Ann. Chim. Phys.* 59, 367; also *Ann. Pharm.* 15, 67.
D'ARCET. *L'Institut.* 1835, No. 105; also *J. pr. Chem.* 5, 28.
E. KOPP. *N. J. Pharm.* 6, 110; also *Compt. rend.* 18, 871; also *J. pr. Chem.* 33, 182.

Faraday's Iodide of Hydrocarbon, Iodide of Elayl, Hydriodate of Acetylic Iodide, Iodkohlenwasserstoff, Iodelayl, iodwasserstoffsaures Iodacetyl, Zweifach-Iodeine; Iodure élaylique, Hydriodate d'Iodure d'Aldehydène [*Schevine*]. — Discovered by Faraday in 1821.

Formation and Preparation. 1. Iodine exposed to the sun in a bottle filled with olefiant gas, gradually condenses the gas, without pre-

ducing hydriodic acid, and forms crystals which may be freed from excess of iodine by means of aqueous potash. (Faraday.)

The iodine granules first become semifluid, then give off red-brown vapours, and after four hours' exposure to daylight, form colourless needles of the compound. After 18 days' action, however, other products are formed; at the bottom of the vessel there collects a blackish green liquid, which sinks in water without dissolving, but when heated with a few drops of water, is resolved with slight explosion, into olefiant gas and a yellowish red volatile liquid. The blackish green liquid, when heated alone, gives off first olefiant gas, then hydriodic acid, then the above-mentioned yellowish red liquid, and also a black liquid which sinks to the bottom of the water in the receiver. If the fluid portion be drained off from the dark green liquid, and Faraday's crystalline compound dissolved out of the residue by boiling alcohol, there remains a green or greenish black, amorphous iodide of hydrocarbon, which was remarked some time ago by Kemp. This compound is lighter than oil of vitriol; destitute of taste and smell; melts and decomposes at the same time; does not dissolve either in alcohol or in ether; and may therefore be separated from the crystals of Faraday's compound which adhere to it, by boiling with alcohol; it burns with a bright flame. When subjected to dry distillation, it yields a dark red-brown liquid, having the odour of *Asafœtida*. (Inglis, *Phil. Mag. J.* 8, 14; also *J. pr. Chem.* 7, 401.)

2. Faraday's compound is produced in the shade as well as in sunshine, but much more slowly unless the action be assisted by heat. To prepare the compound without the aid of sunshine, purified olefiant gas is passed into a long-necked flask in which iodine is heated to 50° or 60°. The iodine melts, turns brown, and yields a sublimate of yellowish needles, which become perfectly white when more olefiant gas is introduced. They are washed, first with water containing potash or ammonia, then with pure water, and afterwards dried in vacuo, during which they acquire a slight yellow tint. But by heating them to 45° or 50° in a stream of dry air and in contact with a small quantity of mercury, the compound may be made to sublime in colourless needles. (Regnault.) — 3. Vapour of iodide of ethyl is passed through a narrow glass tube heated to dull redness; the iodide of ethylene which is deposited in the tube and still has a brown-red colour, freed from uncombined iodine by means of boiling potash-ley; the fused residue dissolved after solidification, in boiling alcohol; the yellowish white needles which form on cooling, subjected to strong pressure and finally exposed to the air, whereupon they become quite white. (E. Kopp.) — 4. When the gas obtained by the dry distillation of coal is passed slowly and continuously over iodine, a number of products are formed, and amongst them, iodoform and iodide of ethylene; the latter may be dissolved out by alcohol and precipitated by aqueous potash. (Johnston, *Phil. Mag. J.* 17, 1; also *J. pr. Chem.* 21, 115.)

Properties. Colourless prisms and tables. (Faraday.) Colourless silky needles. (Regnault.) Friable (Faraday); flexible and of sp. gr. 2·07. (E. Kopp.) Melts at 73° (Regnault), at 70° (E. Kopp), to a yellowish oil which solidifies in the crystalline state on cooling. (Kopp.) Sublimes without decomposition below 80°. Has an aromatic odour and sweetish taste. (Faraday.) The vapour excites tears and produces headache. (Regnault.)

				Faraday.	Regnault.	D'Arcet.	E. Kopp.
4 C	24	8·57		8·85	8·58	8·51	8·40
4 H	4	1·43		1·43	1·46	1·60	1·57
2 I	252	90·00				89·89	89·70
$C^4H^4I^2$	280	100·00				100·00	99·67

May also be regarded as C^4H^3I,HI.

Decompositions. 1. Biniodide of ethylene is resolved by heat into iodine and olefiant gas. (Faraday.) The decomposition takes place slowly in vacuo, even at ordinary temperatures, somewhat more quickly if assisted by daylight; when heated above the melting point, the compound turns brown and decomposes completely. (Regnault.) It begins to decompose at 84°, assuming a yellowish red colour, which becomes continually deeper as the iodine separates. At a still higher temperature it volatilizes, and is partly resolved into iodine and combustible gas; but a portion sublimes unaltered,—excepting that it is browned by iodine. (E. Kopp.) — 2. In the flame of alcohol the compound decomposes, with evolution of iodine and hydriodic acid. (Faraday.) — 3. When chlorine gas is passed over the crystals, they become heated and yield chloride of ethylene ($C^4H^4Cl^2$), together with yellow crystals of terchloride of iodine; bromine also makes the crystals hot and forms bromide of ethylene ($C^4H^4Br^2$), together with bromide of iodine. (Regnault.) — 4. Strong nitric acid immediately gives off nitrous vapours and separates iodine. (E. Kopp.) 5. The compound immersed in oil of vitriol decomposes between 150° and 200°. (Faraday.) — 6. When boiled with a concentrated aqueous solution of potash, it evaporates for the most part unaltered, but a small portion is resolved into olefiant gas and iodine, which remains with the potash. (Kopp.) With alcoholic potash, on the contrary, it decomposes even at ordinary temperatures, giving off a gas which smells like garlic (probably a mixture of olefiant gas and vapour of C^4H^3I). After the decomposition has ceased at ordinary temperatures, it recommences between 50° and 60°, and goes on till the end. (Regnault.) When the compound is boiled with alcoholic potash, part of it is resolved into olefiant gas and iodine, which remains with the potash, and the rest into C^4H^3I and iodide of potassium. (E. Kopp.) — 7. The vapour passed over red-hot copper (Faraday) or iron (Kopp) yields a metallic iodide and olefiant gas. Potassium produces this decomposition even at ordinary temperatures. (Regnault.) — 8. The compound heated with cyanide of mercury yields iodide of cyanogen and combustible gas. (Kopp.) Probably thus:

$$C^4H^4I^2 + C^2NHg = HgI + C^2NI + C^4H^4.$$

Combinations. Biniodide of ethylene is insoluble in *Water*.

It dissolves in *Alcohol*, but less freely than the corresponding bromine and chlorine compounds. (Regnault.)

Its alcoholic solution mixed with that of *Cyanide of Mercury*, yields white needles, which fuse when heated, are not decomposed at 80°; but are resolved at higher temperatures into iodide of mercury, iodide of cyanogen, olefiant gas, and a small quantity of charcoal; probably, therefore, $C^4H^4I^2,HgCy$. (E. Kopp.)

Bromide of Ethyl. C^4H^4,HBr.

SERULLAS. *Ann. Chim. Phys.* 34, 99; also *Schw.* 49, 241; also *Pogg.* 9, 338; also *N. Tr.* 15, 2, 12.
LÖWIG. *Ann. Pharm.* 3, 291.

Hydrobromic ether, Hydrobromnaphtha, Bromwasserstoffäther, Bromäthyl, Bromvinafer, Ether hydrobromique s. *bromhydrique, Bromure d'Éthyle.* [*Lamavine*]. — Discovered by Serullas in 1827.

Preparation. 1. One part of phosphorus and 40 pts. alcohol of 38° Bm. are introduced into a tubulated retort, and 7 to 8 pts. of bromine gradually added, whereupon the mixture becomes heated and hydrobromic and phosphorous acids are produced; the tubulus is then closed, the mixture distilled at a gentle heat, the distillate collected in a cooled receiver; and the hydrobromic ether separated from it by water, to which, if the distillate contains acid, a small quantity of potash is added. (Serullas.) — 2. Absolute alcohol gradually mixed in a distillatory apparatus with a treble quantity of bromine and heated from without towards the end of the process, yields a distillate consisting of two layers. (p. 215.) The lower reddish stratum, which consists of bromide of ethyl, a small quantity of bromide of carbon (C^2Br^2), and free bromine, is freed from the latter by agitation with dilute potash till it loses its colour, and then from bromide of carbon by distillation. (Löwig.)

Properties. Transparent and colourless liquid, heavier than water. (Serullas.) Sp. gr. 1·40. (Löwig.) 1·4733 at 0°. (Pierre.) Vapour-density = 3·754. (R. Marchand, *J. pr. Chem.* 38, 188.) Very volatile. Boiling point 40·7° when the barometer stands at 757 mm. (Pierre.) Has a strong ethereal odour and a pungent taste. (Serullas.) According to Löwig, its taste is strongly and disagreeably sweetish, with a somewhat burning aftertaste. — The vapour, when inhaled, exerts an anæsthetic action, like chloroform. (Robin, *Compt. rend.* 32, 649.)

Calculation.					Vol.		Density.
4 C	24	....	22·02	C-vapour	4	....	1·6640
5 H	5	....	4·59	H-gas	5	....	0·3465
Br	80	....	73·39	Br-vapour	1	....	5·5465
C^4H^5Br	109	....	100·00	C^4H^5Br-vapour	2	....	7·5570
					1	....	3·7785

Decompositions 1. Vapour of hydrobromic ether passed through a glass tube at a low red heat is resolved into olefiant gas and hydrobromic acid gas; if the tube be more strongly ignited, charcoal is deposited. (Löwig.) — 2. It burns with difficulty, but with a beautiful green flame which does not smoke; a strong odour of hydrobromic acid is at the same time evolved. (Löwig.) — It is not decomposed by nitric acid, oil of vitriol, or potassium. (Löwig.) — ¶ With *Ammonia* it yields hydrobromate of ethylamine:

$$NH^3 + C^4H^5Br = C^4H^7N,HBr;$$

Similar with *Ethylamine*, it forms hydrobromate of *Diethylamine;* and with the latter, hydrobromate of *Triethylamine.* With *Aniline*, $C^{12}H^7N$,

it yields the hydrobromate of *Ethylaniline* or *Ethylophenylamine*, $C^{16}H^{11}N,HBr$. (Hofmann, *vid.* VII. 179, 180.) ¶.

Combinations. — Bromide of ethyl is but sparingly soluble in *Water*, to which however it imparts its taste and odour. (Löwig.)

It mixes in all proportions with *Alcohol* and *Ether*. (Löwig.) It is precipitated from the alcoholic solution by water. (Serullas.)

Bibromide of Ethylene. C^4H^4,Br^2.

BALARD. *Ann. Chim. Phys.* 32, 375; also *Schw.* 48, 99; also *Pogg.* 8, 469.
LÖWIG. *Das Brom und seine chemischen Verhältnisse.* Heidelb. 1829, 47. — Further, *Pogg.* 37, 552.
REGNAULT. *Ann. Chim. Phys.* 59, 358; also *Ann. Pharm.* 15, 60.
D'ARCET. *L'Institut.* 1825, No. 105; also *J. pr. Chem.* 5, 28.

Bromelayl, bromwasserstoffsaures Bromacetyl, Zweifach-Bromvine, Bromure élaidique, Hydrobromate de Bromure d'Aldehydène. [*Mevine.*] — Discovered by Balard in 1826.

Formation and Preparation. Bromine dropped into olefiant gas absorbs it immediately with evolution of heat, and forms this oily compound. (Balard.) — A small quantity of hydrobromic acid is always formed at the same time, especially towards the end of the operation, even if the olefiant gas evolved from alcohol and oil of vitriol has been previously passed through a strong solution of caustic potash. (Regnault.) — The resulting oil is washed several times with water containing potash, and then rectified alternately over oil of vitriol (with which it blackens strongly the first time) and baryta. (Regnault.)

The same oil, together with free bromine, passes over when the mother-liquor of salt-springs containing bromine is charged with chlorine till it exhibits a yellow colour (II, 273), and then distilled; it may be separated from the free bromine by water. Its formation is probably due to the presence of organic matters in the water [introduced during the *graduation*]. (Balard.) — Hermann (*Schw.* 49, 388), appears to have obtained the same oil from the mother-liquor of the Schönebeck spring. — According to Löwig (*das Brom.* 47), it likewise distils over, together with bromine, in the preparation of bromine by the method of Desfosses (II, 274), and may be immediately recognized by its odour, as soon as the bromine is saturated with potash. Löwig, also, in distilling ether with a large quantity of bromine, obtained, first hydrobromic acid, then a transparent and colourless oil, which, after being purified with caustic potash, exhibited a density of 2·78: this he regarded as bromide of ethylene.

Properties. Crystallizes at 0°, and does not melt till heated above 6° or 7°. (Serullas, *Ann. Chim. Phys.* 39, 228.) Colourless oil, heavier than water, volatile, and having an ethereal odour even more pleasant than that of Dutch liquid. (Balard.) Solidifies at —2·3° in transparent crystals, part however remaining liquid and exhibiting acid properties. (Löwig.) — Crystallizes between —12° and —15°, forming a camphoroïdal

mass. In the liquid state it is mobile and has a density of 2·164 at 21°. Makes grease-spots on paper, which however soon disappear. Boils at 129° under a pressure of 0·762 met. Vapour-density = 6·485. Tastes sweet. (Regnault.) — Sp. gr. 2·128 at 13°. Boiling point 130°. Vapour-density 6·37. Has a very pleasant ethereal odour and a saccharine taste. (D'Arcet.)

			Löwig. *The crystallized portion.*	D'Arcet.	Regnault.
4 C	24	12·76	12·72	13·44	12·80
4 H	4	2·13	2·08	2·32	2·21
2 Br	160	85·11	85·20	84·24	
C^4H^4,Br^2	188	100·00	100·00	100·00	

	Vol.	Density.
C-vapour	4	1·6640
H-gas	4	0·2772
Br-vapour	2	11·0930
C^4H^4,Br^2-vapour	2	13·0342
	1	6·5171

May also be regarded as C^4H^3Br,HBr.

Decompositions. The vapour of this compound passed through a red-hot glass tube, is resolved into hydrobromic acid and carbon. (Balard.) [Other products must be formed at the same time]. — 2. When set on fire by a flaming body, it burns with a very smoky flame, giving off strongly acid vapours. (Balard.) — 3. Chlorine does not decompose it under the influence of diffused daylight; but in sunshine decomposes it slowly, colouring it yellow and giving off acid vapours, without forming C^4Cl^6. (Regnault.) Bromine does not act on it under the influence of the sun's rays, not even in 5 months. (Regnault, D'Arcet.) Oil of vitriol also exerts no perceptible action upon it. (Regnault.) — Alcoholic potash decomposes the oil, yielding bromide of potassium, water, and gaseous bromide of acetyl; but aqueous potash has no action upon it. (Regnault.)

$$C^4H^4Br^2 + KO = C^4H^3Br + HO + KBr.$$

A mixture of alcoholic bromide of ethylene and concentrated alcoholic potash yields a copious precipitate of bromide of potassium, and gives off with effervescence gaseous bromide of acetyl, recognizable by its peculiar odour; this gas is all given off between 30° and 40°. (Regnault.) — 5. Potassium exerts a decomposing action even at ordinary temperatures; when heated it sets fire to the compound. (Regnault.)

Bromide of ethylene dissolves in *Ether*, *Alcohol*, and strong *Acetic Acid*. Hermann.

Chloride of Ethyl. $C^4H^5Cl = C^4H^4,HCl$.

Pott. *Collect. prim. Obs. et Animadv.* 1739, 117.
Rouelle, Courtanvaux, *Journ. d. Sçavans*, 1759, 405, 549.
J. Fr. Gmelin, *Crell. Chem. J.* 4, 11.
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BASSE. *Crell. Ann.* 1801, 1, 361. — *A. Gehl.* 2, 199.
GEHLEN. *A. Gehl.* 2, 206.
PFAFF. *N. Gehl.* 5, 333.
THENARD. *Mém. de la Soc. d'Arcueil*, 1, 115, 140, and 337; abstr. *N. Gehl.* 4, 24. — *Ann. Chim.* 63, 49; also *A. Tr.* 1, 163.
P. F. G. BOULLAY. *Ann. Chim.* 63, 90; also *N. Gehl.* 4, 37; abstr. *Gilb.* 44, 281. — *Bull. Pharm.* 1, 147.
ROBIQUET & COLIN. *Ann. Chim. Phys.* 1, 348; also *Schw.* 19, 149.
REGNAULT. *Ann. Chim. Phys.* 71, 355; also *Ann. Pharm.* 33, 310; also *J. pr. Chem.* 19, 192.

Light Hydrochloric ether, leichte Salznaphtha, leichter Salzäther, Chlorwasserstoffäther, Chloräthyl, Chlorvinafer, Éther muriatique, hydrochlorique s. chlorhydrique, Chlorure d'Éthyle. [Lakavine.] — The preparation of hydrochloric ether from alcohol and various metallic chlorides was known to some of the older chemists, especially Rouelle; from alcohol and hydrochloric acid, it was first obtained by Basse, then by Gehlen, Thénard and Boullay. Its true composition was first ascertained by Robiquet & Colin.

Formation. 1. From alcohol and hydrochloric acid.

$$C^4H^6O^2 + HCl = C^4H^5Cl + 2HO.$$

The affinity of the hydrochloric acid which is in excess for the water influences the formation of the water as well as that of the hydrochloric ether; but the latter is produced more abundantly in proportion as the acid contains less water. — Alcohol saturated with hydrochloric acid gas forms chloride of ethyl, even at ordinary temperatures, so that the liquid, which fumes at first, gradually acquires an agreeable odour, and on the addition of water separates into two layers, the upper of which is chloride of ethyl, and the latter a mixture of water, alcohol, and hydrochloric acid (Boullay.) — 2. From alcohol and chloride of phosphorus, chloride of sulphur, chloride of aluminum, bichloride of vanadium, terchloride and pentachloride of antimony, chloride of bismuth, chloride of zinc (water being completely excluded), bichloride of tin, sesquichloride of iron, and protochloride and bichloride of platinum. The chloride of ethyl thus obtained is generally contaminated with common ether. (VII. 246–253). — 3. By distilling acetic ether with hydrochloric acid (Duflos), and by the action of chlorine on iodide of ethyl. (Dumas & Stas.)

Preparation. 1. Absolute or very highly rectified alcohol is saturated with hydrochloric acid gas; the mixture distilled at a very gentle heat; and the vapour of the chloride of ethyl, which boils as low as 12·5°, condensed in a receiver surrounded by a freezing mixture. (Basse, Boullay.) The mixture begins to boil at 7°. To avoid loss, it is best to use a tubulated receiver connected with two Woulfe's bottles, the first of which is surrounded by the freezing mixture, and the second partly filled with water. The vapour of the hydrochloric ether may also be first passed through a Woulfe's bottle not cooled, but filled with a solution of common salt to wash it. 100 pts. of very highly rectified alcohol take up from 167 to 175 pts. of hydrochloric acid gas and afterwards yield by distillation 20 pts. of hydrochloric ether. (Boullay.) — 2. A mixture of equal measures of absolute alcohol and the strongest hydrochloric acid is

Properties.—Thin, transparent, and colourless liquid which does not solidify at −29°. (Thénard.) Sp. gr. (as prepared by 2) 0·874 at 5° (Thénard); (3), 0·845 (Gehlen); 0·869 at 0° (Pfaff); (by 4, with $SnCl^2$), 0·805 (Gehlen); 0·9214 at 0°. (Pierre.) — Boiling point of (2) = 12° (Thénard); of (3) = 12·5° (Gehlen); according to Pierre, the boiling point is 11°, when the barometer stands at 755·8 mm.—The presence of common ether in the chloride of ethyl prepared by (3) and still more in that prepared by (4), must lower the specific gravity and raise the boiling point. Vapour-density 2·219 (Thénard). Refracting power of the vapour (I, 95). Neutral. Has a pungent ethereal odour, a sweetish, aromatic taste, with a somewhat alliaceous after-taste.

				Thénard.		Vol.	Density.
4 C	24·0	37·27	36·61		C-vapour	4	1·6640
5 H	5·0	7·76	10·64		H-gas	5	0·3465
Cl	35·4	54·97			Cl-gas	1	2·4543
C^4H^5Cl	64·4	100·00			C^4H^5Cl-vapour	2	4·4648
						1	2·2324

May also be regarded as C^4H^4,HCl or C^4ClH^3,H^2.

Decompositions. The vapour dried as completely as possible, and then passed through a *porcelain tube at a low red heat*, is resolved into equal volumes of hydrochloric acid and olefiant gas. (Thénard, *Traité de Chimie.*) If the tube be very strongly ignited and filled with fragments of porcelain, hydrochloric acid is obtained together with a light, easily combustible gas and a large quantity of charcoal, which soon stops up the tube. The quantity of hydrochloric acid thus obtained corresponds with that which disappears in the preparation of the chloride of ethyl. (Thénard, Robiquet, and Colin.) — 100 vol. of the gas obtained in this decomposition contain 37 vol. hydrochloric acid gas and 63 vol. of a mixture of about 39 vol. marsh-gas and 61 vol. hydrogen. — 2. Chloride of ethyl *burns* quickly in the air, with a green and yellow smoky flame, giving off hydrochloric acid, which may be recognized by its odour and by forming a precipitate of chloride of silver when the combustion takes place over a solution of silver. (Scheele.) — 3. *Chlorine gas* decomposes chloride of ethyl, with great evolution of heat and formation of hydrochloric acid. (Thénard.) — If the action be too rapid, the liquid takes fire and deposits soot; but if the action be slow, and ultimately assisted by heat and sunshine, the chloride of ethyl is converted into the substitution-products $C^4H^4Cl^2$, $C^4H^3Cl^3$, $C^4H^2Cl^4$, C^4HCl^5, and finally into sesquichloride of carbon, C^4Cl^6. (Regnault.)—Chloride of ethyl exposed to the sun in a bottle filled with dry chlorine, takes fire after a few seconds, and burns with a red flame, which spreads from below upwards, depositing charcoal and breaking the flask. If, on the other hand, the liquid in the atmosphere of chlorine be exposed, first to diffused daylight and afterwards to direct sunshine, it is converted by degrees into sesquichloride of carbon. (Laurent, *Ann. Chim. Phys.* 64, 328.)—In weak daylight chlorine acts slowly upon hydrochloric ether; but if the action be set up by exposure to the sun for a short time, it will go on by itself even in the dark; and in daylight, if the hydrochloric ether is in excess, the compound $C^4H^4Cl^2$ is obtained. This compound, if exposed to the further action of chlorine, first in daylight and afterwards in sunshine, is converted, first into $C^4H^3Cl^3$, then into $C^4H^2Cl^4$, then into C^4HCl^5, and ultimately into C^4Cl^6 (Regnault, *Ann. Chim. Phys.* 71, 355);

$$C^4H^5Cl + 2Cl = C^4H^4Cl^2 + HCl;$$
$$C^4H^4Cl^2 + 2Cl = C^4H^3Cl^3 + HCl;$$
$$C^4H^3Cl^3 + 2Cl = C^4H^2Cl^4 + HCl;$$
$$C^4H^2Cl^4 + 2Cl = C^4H\,Cl^5 + HCl;$$
$$C^4H\,Cl^5 + 2Cl = C^4Cl^6 + HCl;$$

For further details see the substitution-compounds.

4. Cold *nitric acid* of sp. gr. 1·3, exerts no action on chloride of ethyl; when the vapour of that compound is passed through the boiling acid, hydrochloric acid is evolved, together with a small quantity of nitrous ether. (Thénard, Boullay.)—5. Anhydrous *sulphuric acid* absorbs the vapour of hydrochloric ether abundantly, and converts it into a liquid, which fumes in the air, boils at 130°, and passes over partly undecomposed, whilst the residue turns brown and gives off sulphurous acid. If the fuming liquid be mixed with water, an oil separates out, which is but little heavier than water—smells like garlic—excites a copious flow of tears—dissolves iodine and is coloured purple thereby, and dissolves sparingly in cold, but much more abundantly in hot water, forming a solution which, if the oil has been previously well washed, precipitates silver but not baryta salts. The watery liquid from which the oil has separated contains an acid analogous to sulphovinic acid, which, if mixed hot with aqueous chloride of barium, yields silky needles of a baryta-salt on cooling. (Kuhlmann, *Ann. Pharm.* 33, 108.)—Oil of vitriol likewise absorbs vapour of chloride of ethyl, but does not afterwards yield an oil on addition of water. (Kuhlmann.) Oil of vitriol does not exert any decomposing action at medium temperatures, but when the vapour of hydrochloric ether is passed through it at a high temperature, hydrochloric acid gas is evolved (Thénard), together with olefiant gas and ultimately also with sulphurus acid. (Boullay.)—6. In an aqueous solution of *nitrate of silver*, chloride of ethyl, whether in the gaseous or liquid state, forms no precipitate at first, a very slight one after an hour, and even in three months but a small quantity of chloride of silver (Thénard, Boullay); according to Thénard, it acts in a precisely similar manner on mercurous nitrate, but according to Boullay, it immediately throws down a large quantity of calomel from a solution of that salt.—7. *Ammoniacal gas* and the aqueous solution of ammonia act but very slowly at ordinary temperatures on chloride of ethyl, either in the gaseous or liquid state, taking up a small quantity of chlorine from it. (Thénard.) 5 pts. of aqueous ammonia take all the chlorine from 2 pts. of chloride of ethyl in the course of a few days. (Boullay.) A mixture of 1 vol. chloride of ethyl vapour and 2 vol. ammoniacal gas heated over the flame of a spirit-lamp, soon diminishes in volume, deposits a large quantity of sal-ammoniac, and after being heated for some time, leaves a mixture of ammoniacal and olefiant gas. (Dumas & Stas, *Ann. Chim. Phys.* 73, 154; also *Ann. Pharm.* 35, 163):—

$$C^4H^5Cl + NH^3 = C^4H^4 + NH^4Cl.$$

8. Aqueous *potash* at ordinary temperatures takes but a small quantity of chlorine from chloride of ethyl, even in the course of three months. Even when the vapour is passed for 15 hours through potash-ley heated to 80°, only a small quantity of the hydrochloric ether is decomposed and a small quantity of chloride of potassium formed, but no alcohol. (Thénard.) According to Boullay, the vapour of hydrochloric ether passed through a bent tube into potash-ley heated in a tubulated retort is almost wholly decomposed, so that chloride of potassium is formed and alcohol having the taste and smell of rum distils over:

$$C^4H^5Cl + HO + KO = C^4H^6O^2 + KCl.$$

Combinations. Chloride of ethyl dissolves in 50 pts. of water according to Gehlen, and in 60 pts. according to Pfaff; 1 vol. water at 18° absorbs 1 vol. vapour of hydrochloric ether. (Thénard). The solution, which has a sweet and powerful taste, does not act either on litmus or on a solution of silver.

Pentachloride of Antimony absorbs the vapour of chloride of ethyl with evolution of heat, and forms a colourless liquid which fumes in the air, and in a dry atmosphere solidifies to a crystalline mass; this, however, gradually becomes liquid and brown, and slowly deposits crystals of terchloride of antimony, whereupon water throws down a brown oil from the brown mother-liquid. (Kuhlmann.)

Bichloride of Tin likewise yields, with evolution of heat, a liquid which fumes in the air, and when set aside over lime under a bell-jar containing air, effloresces on the edge of the basin in plumose vegetations. Water decomposes the compound, separating part of the ether in the undecomposed state, and if the compound is not recently prepared, precipitating a white substance, probably binoxide of tin. (Kuhlmann.)

Sesquichloride of Iron in dry air forms with chloride of ethyl a compound which crystallizes indistinctly, and from which water throws down a large quantity of ferric oxide and separates hydrochloric ether. (Kuhlmann, *Ann. Pharm.* 33, 108.)

Chloride of ethyl agitated with aqueous terchloride of gold, does not take up any chloride of gold.

Chloride of ethyl mixes in all proportions with *Ether* and *Alcohol.* From the latter, according to Funcke (*Br. Arch.* 4, 265), it may be separated by neutral tartrate of potash.

Chloride of ethyl dissolves oils both fixed and volatile, also several resins and colouring matters, *e. g. coccus-red.*

Heavy Hydrochloric Ether.

SCHEELE. *Opuscula*, 2, 135. — WESTRUMB, *Kl. Chem. Abhandl.* 1, 2, 57. — TROMMSDORFF, *Scher. J.* 3, 378. — GEHLEN, *A. Gehl.* 2, 227. — THÉNARD, *Mém. de la Soc. d'Arcueil*, 1, 147; 2, 25. — BERTHOLLET, *Ann. Chim. Phys.* 1, 426. — ROBIQUET & COLIN, *Ann. Chim. Phys.* 2, 208. — DESPRETZ, *Ann. Chim. Phys.* 21, 437. — A. VOGEL, *Kastn. Arch.* 7, 343. — PFAFF. *Schw.* 55, 204. — LIEBIG, *Mag. Pharm.* 34, 49. — *Ann. Pharm.* 1, 221; also *Pogg.* 24, 244, and 284.

Schwere Salzäther, schwere Salznaphtha, schweres Salzöl, Chloräther, Ether chlorique. — First prepared by Scheele and Westrumb. Produced by the action of chlorine on considerable quantities of alcohol or ether; according to Wöhler, also in the decomposition of alcohol by chlorochromic acid.

Preparation. 1, Chlorine gas evolved from 35 pts. common salt, 9 pts. manganese, 16 pts. oil of vitriol, and 16 pts. water is passed into 6 pts. alcohol; and the resulting compound ether, which amounts to $\frac{1}{6}$ of the alcohol, is purified by water and potash. (Scheele, Thénard.) Vogel saturates the alcohol with chlorine without heating it (in which case the

addition of water throws down but a small quantity of the compound ether), neutralizes with carbonate of lime, distils, and throws down the compound ether from the distillate by adding 2 or 3 vol. of water. Pfaff saturates cold alcohol of sp. gr. 0·828 with chlorine gas; removes the free chlorine by lead and the hydrochloric acid by chalk; decants the layer of heavy hydrochloric ether which rises to the top, and washes it repeatedly with water: acetic ether however remains mixed with it. — Liebig saturates the alcohol with chlorine at ordinary temperatures, mixes it with an equal bulk of water, and without separating the precipitated compound ether, adds to it finely pounded manganese, which appears to dissolve at first, forming a dark green liquid; but in a few seconds this liquid changes to light brown and becomes heated, so that it takes fire and burns with a red flame, unless the vessel be surrounded with cold water or the mixture diluted therewith. If the mixture be then distilled, acetic ether passes over first, then pure, neutral, heavy hydrochloric ether, and at last C^2Cl^4 also sublimes. (Liebig.) — 2. Scheele saturates 3 pts. of alcohol with hydrochloric acid gas evolved from 2 pts. common salt and 2 pts. sulphuric acid, and distils this alcohol with 3 pts. of manganese. — 3. Scheele distils 3 pts. of alcohol with 1 pt. oil of vitriol, 3 pts. of common salt, and 3 pts. of manganese; — Westrumb, 3 pts. of alcohol with 1 pt. oil of vitriol, 2 pts. common salt, and 1 pt. manganese. — Trommsdorff, 3 pts. alcohol with 1 pt. oil of vitriol, 2 pts. common salt, and ½ pt. manganese; — Gehlen, 10 pts. alcohol with 10 pts. oil of vitriol, 13 pts. common salt, and 6 pts. manganese. The compound ether is separated from the distillate by addition of water, and from free acid by treating it with magnesia or solution of potash. — 4. Brugnatelli (*Scher. J.* 7, 109) distils 1 pt. of alcohol with 1 pt. oil of vitriol and 2 pts. chlorate of potash. — 5. Berthollet, also Robiquet & Colin, pass chlorine gas through ether and precipitate the heavy hydrochloric ether with water.

Properties. Colourless, thin, oily liquid, of sp. gr. 1·084 (Pfaff.), 1·134 (A. Vogel), 1·227 (Liebig). Refracting power 1·0606 (Fraunhofer). According to former statements, it boils below 100°; according to Liebig, at about 112°, but the boiling point is variable. Has a pungent, sweetly aromatic odour, like that of nitrous ether, but, according to Liebig, quite different from that of the oil of olefiant gas. Has an aromatic fiery taste. Does not redden litmus.

Decompositions. 1. This compound when passed through a red-hot tube yields hydrochloric acid. (Thénard.) — 2. Burns with a green and yellow flame, giving off hydrochloric acid. If therefore the flame be blown out after awhile, the residue, according to Liebig, precipitates a solution of silver. — 3. When exposed to light in contact with chlorine gas, it forms sesquichloride of carbon, to judge by the smell — but in much smaller quantity than Dutch liquid — and is converted into a thick liquid rendered turbid by a white substance. (Gm.) — 4. Decomposes in contact with nitric acid, giving off chlorine or hydrochloric acid. (Thénard.) — 5. The compound, as prepared by (5), is charred by oil of vitriol, whereas Dutch liquid is not (Robiquet & Colin); that prepared by (1) becomes turbid and froths up strongly when mixed with cold oil of vitriol, giving off a large quantity of hydrochloric and carbonic acid gas; on heating the mixture, a considerable quantity of charcoal is deposited, and, above 100°, sulphurous acid gas is likewise evolved. (Liebig.) — 6. When the liquid prepared by (1) is shaken up with strong potash and distilled, it gives off

a white, oily liquid, and afterwards water free from alcohol; the dry residue when ignited gives off an empyreumatic odour and yields a needle-shaped sublimate, which burns and produces hydrochloric acid (chloride of carbon?); there remains charcoal, chloride of potassium, and potash. (A. Vogel.) The dry residue contains a brown resin (Liebig.) Heavy hydrochloric ether placed in a retort together with hydrate of potash becomes strongly heated, boils violently, and gives off a peculiar oily body different from itself, having a density of 1·074 and boiling at 104°. A mixture of heavy hydrochloric ether and alcoholic potash deposits chloroform in oily drops on the addition of water. (Liebig.) — The preparation (5) treated with an aqueous solution of carbonate of soda is gradually reduced to $\frac{1}{5}$ of its volume and assumes a yellowish tint; if the residue be mixed with potash and evaporated, a large quantity of carbonaceous matter separates from it, and the soda and potash are found to have taken up a considerable quantity of hydrochloric acid. (Berthollet.) — (5) is more easily decomposed by aqueous alkalis than Dutch liquid. (Robiquet & Colin.)

Combinations. — Heavy hydrochloric ether dissolves very sparingly in water. Two drops of it placed in an ounce of water take several days to dissolve. (Vogel.) — At ordinary temperatures, it dissolves a large quantity of *phosphorus.* — In alcohol it dissolves in all proportions, and is partly precipitated from the solution by water. The ordinary *Spiritus salis dulcis* is a preparation of this kind. It dissolves in all proportions in ether.

Despretz regards heavy hydrochloric ether as a compound of 1 vol. chlorine gas with 2 vol. olefiant gas; according to A. Vogel it is identical with Dutch liquid (p. 376); Berthollet also regards the heavy hydrochloric ether prepared from common ether as a compound of chlorine with olefiant gas; according to Robiquet & Colin, however, the product obtained from alcohol or common ether differs from Dutch liquid by a stronger and more unpleasant taste and odour, greater volatility and inflammability, and by being more easily decomposed by alkalis and carbonized by oil of vitriol.

Heavy hydrochloric ether is probably not a peculiar definite compound, but a mixture in varying proportions of acetic ether, aldehyde, chloral, and perhaps also Dutch liquid, &c. — Liebig (*Ann. Pharm.* 14, 137) found in it a large quantity of aldehyde, which is perhaps the cause of the formation of resin by potash and the charring by oil of vitriol; the chloroform which, according to Liebig, separates out on the addition of alcoholic potash and subsequently of water, points to the presence of chloral. — Regnault (*Ann. Chim. Phys.* 71, 421) suggests also that it contains $C^4ClH^3O^2$ and $C^4Cl^2H^2O^2$.

Monochlorinated Hydrochloric Ether. $C^4H^4Cl^2 = C^4Cl^2H^2,H^2$?

Regnault (1838). *Ann. Chim. Phys.* 69, 193; also *Ann. Pharm.* 33, 310; also *J. pr. Chem.* 19, 195.

Einfachchlorhaltiger Chlorwasserstoffäther, Bichlorvinafer, Aldehydchlorid, Ether hydrochlorique monochloruré.

Preparation. The apparatus used is the same as that for the preparation of monochlorinated methyl-ether (VII. 289), excepting that only

one Woulfe's bottle is required, together with a flask filled with water and surrounded with ice. Into one opening of the glass globe is passed chlorine gas, which must not be in excess, and into the other, vapour of hydrochloric ether evolved by heat from a concentrated mixture of alcohol and hydrochloric acid, and purified by passing first through water, then through oil of vitriol, and lastly again through water. When the chlorine gas is in excess, $C^4H^3Cl^3$ is also formed; this, however, remains in the Woulfe's bottle, whilst the more volatile $C^4H^4Cl^2$ passes over for the most part into the flask surrounded with ice. The apparatus must be exposed to the sun, at least at the beginning of the action; but when the action has once been set up in this manner, it goes on by itself in diffused daylight and even in twilight. The liquid collected in the flask is several times washed with water; and if the chlorine has not been admitted in excess, and consequently no $C^4H^3Cl^3$ has been formed, that in the Woulfe's bottle is also washed; the whole is then rectified in the water-bath, first alone, then in contact with burnt lime, to remove water and hydrochloric acid, the first portion of the distillate which may contain hydrochloric ether, and the last which may contain bichlorinated hydrochloric ether, being set aside. (Regnault.)

Properties. Transparent, colourless, very thin liquid, of sp. gr. 1·174 at 17°. Boils at 64°. Vapour-density 3·478. Smells like oil of olefiant gas, and has a sweet, fiery taste. (Regnault.)

				Regnault.		Vol.	Density.
4 C	24·0	24·29		24·43	C-vapour	4	1·6640
4 H	4·0	4·05		4·16	H-gas	4	0·2772
2 Cl	70·8	71·66		71·12	Cl-vapour	2	4·9056
$C^4H^4Cl^2$	98·8	100·00		99·71		2	6·8468
						1	3·4234

Monochlorinated hydrochloric ether distilled with alcoholic potash passes over for the most part unaltered. But the residue contains a small quantity of chloride of potassium, and on addition of water deposits a brown sticky resin, probably resin of aldehyde. — It may be distilled undecomposed in contact with potassium, the metal retaining its lustre. (Regnault.)

Monochlorinated hydrochloric ether is distinguished from Dutch liquid which is isomeric with it, by its smaller specific gravity, lower boiling point, and difficult decomposibility by potash. Regnault assigns to it the formula $C^4H^4Cl^2$ and to Dutch liquid the formula C^4H^3Cl,HCl. More probably the ether is $C^4Cl^2H^2,H^2$, and the oil either C^4H^3Cl,HCl, as Regnault supposes, or even C^4H^4,Cl^2. According to this view, common ether would be C^4H^3O,H^2 and chloride of ethyl, C^4H^3Cl,H^2.

Oil of Olefiant Gas. $C^4H^4Cl^2 = C^4H^3Cl,HCl$.

Deiman, Troostwyk, Bondt & Lauwerenburgh. *Crell. Ann.* 1794, 2, 200.

Robiquet & Colin. *Ann. Chim. Phys.* 1, 337; 2, 206; also *Schw.* 19, 142; also *Gilb.* 59, 12.

Torin. *Ann. Chim. Phys.* 42, 225; also *Schw.* 60, 479; also *Pogg.* 19, 61.

from alcohol and oil of vitriol is often contaminated (p. 163); for this carbonic acid coming in contact with the chlorine, forms phosgene gas, which is then decomposed by the water into carbonic and hydrochloric acids, and, according to Morin, may be detected even by its odour, provided the gaseous mixture is not very moist:

$$CO + Cl + HO = CO^2 + HCl.$$

If this supposition be correct, an equivalent quantity of carbonic acid must be formed at the same time.

When the olefiant gas is in excess, the oil which condenses exhibits a greyish white turbidity arising from admixture of water; but after a while, it becomes transparent and colourless, more quickly if placed over chloride of calcium. — When the chlorine is in excess, the resulting oil has a greenish yellow colour arising from free chlorine; it likewise emits suffocating acid vapours, has a caustic taste, and gives up its excess of chlorine together with hydrochloric acid to water. (Robiquet & Colin.)

Dutch liquid is also formed by the action of olefiant gas on chlorochromic acid (p. 167), pentachloride of antimony, and protochloride of copper. — Olefiant gas passed through pentachloride of antimony is abundantly absorbed, with evolution of heat and production of a brown colour. As the liquid cools, terchloride of antimony crystallizes out, and the mother-liquor consists of Dutch liquid still containing a small quantity of terchloride of antimony in solution. (Wöhler.) — Chloride of copper fused in olefiant gas gives off large bubbles, which take fire as they burst and burn with a red flame, forming hydrochloric acid and depositing carbon. The Dutch liquid formed at the same time is ultimately converted into a yellowish oil, having an odour like that of turpentine-camphor, and a residue is left consisting of metallic copper and the dichloride. (Wöhler, *Pogg.* 13, 297.)

Preparation. — By passing large quantities of olefiant gas and chlorine in about equal masses into a glass globe, as fast as they condense into an oil; washing the oil with a small quantity of water to remove free chlorine and hydrochloric acid; and distilling it over chloride of calcium to free it from water.

Purification. *a.* If the olefiant gas has merely been purified by caustic potash, it yields a greenish yellow oil, which turns brown when treated with potash, and is blackened by oil of vitriol with evolution of hydrochloric acid. This oil is purified by distillation with a large quantity of water (the watery distillate floating on the top of the oil reduced to three-fourths, contains a large quantity of hydrochloric acid together with acetic ether); then washed with potash-ley, which renders it turbid; then with water till it becomes clear again; then separated from the water, shaken up with 6 or 8 times its volume of oil of vitriol, and distilled (whereupon more hydrochloric acid is evolved, and the oil of vitriol turns brown); the distillate again washed with potash and water; and lastly, shaken up and redistilled with oil of vitriol, which does not eliminate hydrochloric acid or cause the residue to turn brown. (Liebig.) — *b.* The olefiant gas is allowed to predominate; the oil washed with water; rectified alone in the water-bath; dried over chloride of calcium; and kept in a state of ebullition, till the boiling point becomes stationary. — Or *c.* The oil is washed first with water, then with potash-ley; distilled

over chloride of calcium, whereupon heavy hydrochloric ether remains; then rectified in the water-bath, first *per se* — whereby the remaining portion of the heavy hydrochloric ether is left behind — then over hydrate of potash, which becomes slightly brown; then over oil of vitriol, after previous agitation with that liquid; and lastly over finely pulverized baryta. (Dumas.)

d. The oil prepared from olefiant gas, which has been purified both by potash-ley and oil of vitriol, is twice washed with water, with which it becomes strongly heated the first time, even to ebullition; then rectified in the oil-bath *per se;* afterwards over oil of vitriol, which becomes strongly blackened; then over hydrate of potash; then again over oil of vitriol, no further blackening thence ensuing; and, finally, once more over hydrate of potash. The oil, which is still somewhat turbid, becomes clear on agitation with chloride of calcium. — *e.* When the oil purified according to *d* is distilled four times more over oil of vitriol (hydrochloric acid being evolved each time, but the residue blackening only the first time), and alternately therewith, four times over dry baryta, the oil *e* is obtained. (Regnault.)

Guthrie frees the oil from alcohol by repeated distillation over chloride of calcium, then distils it once over oil of vitriol, and mixes it with a concentrated solution of carbonate of potash. As long as the oil retains alcohol, ether passes over in the distillation after the oil, and the residue turns black. (Guthrie.) A. Vogel purifies the oil merely by shaking it up with aqueous carbonate of potash, and then washing with water.

Properties. Thin, transparent, colourless oil. Sp. gr. 1·214 (Vogel); 1·2201 at 7° (Robiquet & Colin); from 1·22 to 1·24 (Morin); 1·247 at 18° (Liebig); (*e*) 1·256 at 12° (Regnault); 1·486 (Guthrie.) Boiling point 66·7 (Robiquet & Colin); 74·4 (Guthrie); 82·4° when it boils alone, but at most 75·66° when boiled with water (Liebig); (*e*) 82·5° at 0·756 met. (Regnault); 85·85° (Despretz, *Ann. Chim. Phys.* 21, 154); (*c*) 85° at 0·77 met.; (*b*) 86° at 0.76 met. (Dumas.) Tension of vapour: 0·06265 met. at 9·3° (Robiquet & Colin); 0·0558 met. at 12·17°. (Despretz.) Vapour-density, 3·4434 (Gay-Lussac); (*b.*) 3·46 (Dumas); (*e.*) 3·478 (Regnault.) The oil does not redden litmus. It possesses a penetrating, agreeably aromatic odour and a pleasant sweetish taste. (Deiman, &c.)

			Liebig.	Dumas.		Regnault.	
			a.	*b.*	*c.*	*d.*	*e.*
4 C	24·0	24·29	23·34	24·6	24·80	21·50	24·35
4 H	4·0	4·05	3·70	4·1	4·13	3·59	4·06
2 Cl	70·8	71·66	71·33	73·0	71·07	72·32	71·41
$C^4H^4Cl^2$	98·8	100·00	98·37	101·7	100·00	97·41	99·82

	Vol.	Density.		Vol.	Density.
C-vapour	4	1·6640	Olefiant-gas	1	0·9706
H-gas	4	0·2772	Cl-gas	1	2·4543
Cl-gas	2	4·9086			
Oil-vapour	2	6·8498		1	3·4249
	1	3·4249			

Morin concluded from his experiments on the formation of the oil and its decomposition in a red-hot tube, that it is C^4H^3Cl, which supposition, however, was soon negatived by the analysis of the oil.

Decompositions. 1. The oil passed through a white-hot tube filled with fragments of porcelain, deposits carbon in the tube, and yields a mixture of 61·39 vol. of hydrochloric acid gas and 38·61 vol. of a combustible gas which burns with a bluish flame. (Robiquet & Colin.) According to these chemists, 100 vol. of this gas exploded with oxygen consume 66 vol. and produce 31 vol. carbonic acid; hence it probably contains 31 vol. marsh-gas and 69 vol. hydrogen. If the porcelain tube is heated only to dull redness, 2 vol. hydrochloric acid gas and 1 vol. combustible gas are obtained, with deposition of charcoal. (Morin.) This combustible gas remains nearly uniform during the whole decomposition. Of the gas obtained at the beginning, 100 vol. detonated with oxygen absorb 160 vol. oxygen and form 60 vol. carbonic acid; of the gas obtained towards the end, 100 vol. consume 150 vol. oxygen and produce 50 vol. carbonic acid. (Morin.) [Hence we may calculate that the first portions of this combustible gas contain 60 vol. marsh-gas to 40 vol. hydrogen, and the latter portions 50 : 50]. — 2. The oil may be *set on fire* by a flaming body, and burns with a green flame which deposits a large quantity of soot and diffuses suffocating vapours of hydrochloric acid. (Rob. & Colin.) The yellowish white flame has a green border at the bottom. (Liebig.) The colour of the flame is emerald-green. (Vogel.)— 3. *Chlorine* acts gradually upon the oil, especially with the aid of light and heat, forming hydrochloric acid and converting it into the substitution-compounds $C^4H^3Cl^3$ and $C^4H^2Cl^4$, and ultimately into sesquichloride of carbon, C^4Cl^6. The oil exposed to the sun in a bottle filled with chlorine, is converted, with formation of hydrochloric acid, into crystals of C^4Cl^6 which sublime (Faraday):

$$C^4H^4Cl^2 + 8Cl = C^4Cl^6 + 4HCl.$$

The same transformation takes place when chlorine is passed through the oil at a temperature near its boiling point. (Liebig.) If the oil immersed in water be saturated with chlorine in a dark place, and the strongly yellow liquid then brought out into the light, it becomes heated, loses its colour, and gives off hydrochloric acid which is absorbed by the water. Chlorine passed through the oil for two days, converts it for the most part into $C^4H^3Cl^3$, (Regnault, *Ann. Chim. Phys.* 69, 159.) If the passage of the chlorine be continued, this compound is converted into $C^4H^2Cl^4$. (Regnault, *Ann. Pharm.* 28, 56.) When dry chlorine gas is continuously passed [in day light?] through the oil contained in a Liebig's bulb-apparatus, first in the cold and afterwards at a gentle heat, hydrochloric acid gas is continually evolved, and after three days, the liquid consists for the most part of $C^4H^2Cl^4$, but contains some crystals of C^4Cl^6. (Laurent.) — 4. Dutch liquid may be mixed with *oil of vitriol* without decomposition, and distilled from it at 100° without alteration; but when dropped into boiling oil of vitriol, it is completely destroyed, without yielding a chloride of carbon. (Liebig.)

5. The oil immersed in *water* and exposed to the sun, is gradually resolved into hydrochloric acid and acetic ether. (Mitscherlich, *Pogg.* 14, 538):

$$3C^4H^4Cl^2 + 4HO = C^8H^8O^4 + 4HCl.$$

It is only the impure oil that yields acetic ether, and it yields that product also when distilled with water; but the perfectly purified oil, when treated with water either in sunshine or by distillation, neither yields acetic ether nor turns sour. (Liebig, *Ann. Pharm.* 1, 218.)

6. *Ammoniacal gas* mixed with the vapour of the oil condenses to

sal-ammoniac, with separation of a combustible gas [and nitrogen ?]. On the cold liquid oil ammoniacal gas has no action. (Robiquet & Colin.) — 7. The oil is but slightly decomposed by aqueous *Potash*, even at high temperatures, but with alcoholic potash it is gradually resolved into chloride of potassium and the compound C^4H^3Cl, which boils even at the heat of the hand. (Regnault.)

$$C^4H^4Cl^2 + KO = C^4H^3Cl + HO + KCl.$$

The oil, when distilled with strong solution of potash, passes over undecomposed at first; but on the application of a stronger heat to the dry residue, a few needles sublime, which are inflammable and yield hydrochloric acid as they burn; an empyreumatic oily odour is emitted, and there remains a carbonaceous mass which likewise contains chloride of calcium. (A. Vogel.) — 8. The oil passed in the state of vapour through a red-hot tube, yields chloride of calcium, charcoal, and distinct crystals of naphthalin. (Regnault.) Hydrogen and carbonic oxide may also be obtained.

9. The alcoholic solution of *Protosulphide of potassium* mixed with the oil, yields bisulphide of ethylene and chloride of potassium:

$$C^4H^4Cl^2 + 2KS = C^4H^4S^2 + 2KCl.$$

The mixture, when kept in a close vessel, assumes a light red colour after some time, but does not form a precipitate, even after several weeks, perhaps because the resulting sulphide of ethylene enters into combination with the undecomposed portion of the sulphide of potassium. On distilling off the alcohol, there remains a brown, deliquescent mass, which has an extremely offensive odour, like that of putrefying animal matter; blackens when heated, giving off an odour like that of the products formed by heating sulphide of ethylene; and, when dissolved in water, yields a yellowish precipitate on exposure to the air, and with acids, a yellowish precipitate which fuses to a brown resin at 100°; acids also cause an evolution of sulphuretted hydrogen. If, on the other hand, the mixture of alcoholic protosulphide of potassium and Dutch liquid be immediately exposed to the air, it becomes less strongly coloured, and yields a white precipitate of $C^4H^4S^2$, mixed perhaps with a little sulphur and $C^4H^4S^4$. (Löwig & Weidmann.) With alcoholic *Tersulphide of potassium*, in a close vessel, the oil forms a yellowish precipitate of $C^4H^4S^{10}$. That the precipitate does not consist of $C^4H^4S^6$,($C^4H^4Cl^2 + 2KS^3 = C^4H^4S^4 + 2KCl$) is explained by Löwig & Weidmann, on the supposition that protosulphide of potassium is formed at the same time:

$$C^4H^4Cl^2 + 4KS^3 = C^4H^4S^{10} + 2KS + 2KCl.$$

The supernatant liquid assumes a reddish colour, probably because a compound of protosulphide of potassium with bisulphide of ethylene is formed at the same time. — The mixture of the oil with alcoholic *Pentasulphide of potassium*, if kept from contact with the air, also yields after awhile the precipitate of $C^4H^4S^{10}$; but if the pentasulphide of potassium has not been added in excess, the supernatant liquid remains colourless.

$$C^4H^4Cl^2 + 2KS^5 = C^4H^4S^{10} + 2KCl.$$

An alcoholic solution of *sulphide of hydrogen and potassium* mixed with Dutch liquid yields chloride of potassium and hydrosulphate of sulphide of ethylene, $C^4H^4S^2 + 2HS$:

$$C^4H^4Cl^2 + 2(KS,HS) = C^4H^6S^4 + 2KCl.$$

The mixture, which remains colourless, soon deposits crystals of chloride of potassium, and if then distilled, yields the above-mentioned compound together with alcohol and undecomposed Dutch liquid; the liquid which remains in the retort deposits an oil which solidifies on cooling, consists of $C^4H^5S^4$, and is probably formed by access of air. — If the mixture of alcoholic sulphide of hydrogen and potassium and Dutch liquid be exposed to the air, it deposits, together with the crystals of potassium, a white, flocculent mixture of $C^4H^4S^4$ and $C^4H^5S^4$, which melts at a gentle heat. (Löwig & Weidmann, *Pogg.* 49, 123.)

10. Potassium does not act on the vapour of the oil at ordinary temperatures; but when heated in the vapour, it becomes red-hot, causes a precipitation of carbon, and forms apparently a small quantity of naphthalin. (Regnault.) When heated in contact with the liquid compound, the potassium swells up to a white porous mass, and gives off in continually increasing quantity a mixture of hydrogen gas and vapour of C^4H^3Cl (Liebig, *Ann. Pharm.* 14, 37):

$$C^4H^4Cl^2 + K = C^4H^3Cl + H + KCl.$$

The gas which goes off with the hydrogen was formerly supposed by Liebig and Dumas to be olefiant gas. — The porous mass is saturated with undecomposed oil, which when treated with water separates out in a milky state, while the chloride of potassium dissolves. (Liebig.)

Combinations. Oil of olefiant gas dissolves very sparingly in *Water*, more readily, according to Morin, when hydrochloric acid is present.

At a moderate heat, it dissolves a large quantity of *Phosphorus*. (Vogel.)

The solution of *Chloriodoform* in Dutch liquid is heavier than oil of vitriol. On distilling it, the Dutch liquid passes over first; and if it be then poured upon a piece of red-hot porcelain, no violet vapours are given off. On exposure to the air for a few days, it becomes reddish, and in contact with chlorine gas slightly yellow. (Serullas, *Ann. Chim. Phys.* 25, 316.)

The oil dissolves in *Alcohol*, and doubtless, also, in many other liquids of similar nature.

According to Despretz (*Ann. Chim. Phys.* 21, 4, 38), chloride of iodine, by taking up a small quantity of olefiant gas, is converted into a liquid of agreeable taste and odour, which solidifies at 0° in crystalline laminæ; and after taking up more olefiant gas, solidifies at ordinary temperatures into a crystalline compound. [Probably a mixture.]

Fluoride of Ethyl? C^4H^5F?

Strong alcohol saturated with the vapour of the acid evolved from fluor spar and oil of vitriol in glass vessels till it fumes, and then distilled, does not yield any ethereal product. If the distillate be several times charged with the acid vapours and distilled over peroxide of manganese, a small quantity of an ethereal liquid is obtained, having an odour like that of nitrous ether. (Scheele, *Opusc.* 2, 137.)

3 pts. of fluorspar distilled in a glass retort with a mixture of 2 pts. absolute alcohol and 2 pts. oil of vitriol, give off a gas which smells of phosphuretted hydrogen and burns with a blue flame, emitting fumes of

hydrofluoric acid, — and a distillate, which when rectified to half its volume, yields an acid, ethereal liquid, which does not diminish much in bulk on being mixed with water, and when mixed with soda, solidifies to a jelly from separation of silica. This liquid yields by distillation a liquid very much like common ether, of sp. gr. 0·720, but tasting like bitter almonds. (Gehlen, *A. Gehl.* 2, 351.)

When 1 pt. of alcohol, contained in a leaden vessel surrounded with ice and salt, is saturated with the hydrofluoric acid evolved by heating in a leaden retort a mixture of 1 pt. fluorspar and 2 pts. oil of vitriol—this liquid (described on page 265) distilled in leaden vessels till only $\frac{1}{4}$ has gone over—and the distillate mixed with twice its bulk of water—a colourless ethereal liquid rises to the top, which has a peculiar taste and odour something like horse-radish, burns with a bluish flame, corrodes the glass vessel even during the act of separation, and is itself decomposed at the same time. — If the alcohol after saturation with hydrofluoric acid be distilled more completely, and the resulting distillate again distilled with $\frac{1}{4}$ of the first quantity of oil of vitriol, a yellowish distillate is obtained which has a pungent odour like that of cat's urine, and if it gets under the finger-nails, produces pain and inflammation just as hydrofluoric acid does. (Reinsch. *J. pr. Chem.* 19, 314.)

Telluride of Ethyl or Tellurethyl. $C^4H^5Te = C^4H^4,HTe$.

WÖHLER (1840.) *Ann. Pharm.* 35, 111; also *Pogg.* 50, 404; also *J. pr. Chem.* 20, 371. — Further: *Ann. Pharm.* 84, 69.

MALLET. *Ann. Pharm.* 79, 223; abstr. *J. pr. Chem.* 54, 135; *Chem. Soc. Qu. J.* V, 71.

Hydrotelluric ether, Tellurwasserstoffäther, Tellurvinafer, Telluräthyl, Ether hydrotellurique.

Telluride of sodium, prepared by igniting tellurium or native telluride of bismuth with charcoal and carbonate of soda (or telluride of potassium, obtained by igniting pulverized tellurium with burnt tartar), is introduced in the dry state into a retort already containing a warm solution of sulphovinate of baryta or potash, and the mixture heated. Telluride of ethyl then passes over together with water, the action being at first attended with great frothing.

¶ Wöhler's latest directions for the preparation of this compound are as follows: Telluride of potassium is prepared by mixing 1 pt. of tellurium powder with 10 pts. of burnt tartar; introducing the mixture into a porcelain retort fitted with a glass tube bent downwards at right angles; heating the retort to redness for 3 or 4 hours, as long indeed as carbonic oxide continues to escape; and then introducing the end of the bent tube into a flask filled with carbonic acid gas, to prevent access of air. As soon as the mixture is quite cold, a concentrated solution of sulphovinate of potash (3 or 4 pts. of the solid salt to 1 pt. of tellurium), prepared with water freed from air by boiling, is poured into the retort, which is then tightly corked; and the whole heated for some time, with constant agitation, to 40° or 50°. The resulting purple solution, together with the undissolved portion, is then quickly poured into a flask previously filled with carbonic acid gas; the retort again filled with the same gas; a small quantity of the solution of sulphovinate poured into it

(a portion having been kept back for the purpose); the retort again closed; and the digestion repeated. These precautions are necessary to prevent loss of telluride of potassium by oxidation. The flask is then connected with a condensing tube and receiver, and the mixture kept constantly in a state of gentle ebullition. The flask then becomes filled with the yellow vapour of tellurethyl, and that compound distils over together with water, in which it sinks in drops. Finally, when about $\frac{5}{6}$ of the monotelluride of ethyl has passed over, a small quantity of bitelluride is likewise obtained, differing from the former by its black-red colour. (*Ann. Pharm* 84, 79.) ¶.

Deep yellowish red liquid, heavier than water, and boiling below 100°. Has a strong, very persistent, and extremely disgusting odour, like that of sulphide of ethyl and telluretted hydrogen. It appears to be very poisonous. Its vapour has a deep yellow colour.

			Wöhler.
4 C	24	25·80	
5 H	5	5·38	
Te	64	68·82	68·75
C^4H^4,HTe	93	100·00	

Telluride of ethyl is very inflammable, and burns with a clear, white flame, bordered with light blue, giving off thick white fumes of tellurous acid. Remains unaltered under water, but when exposed to the air, it becomes covered with a yellowish and afterwards with a white film, and is ultimately converted into a white, earthy mass. In sunshine, this oxidation takes place much more quickly, and is attended with slight fuming; but no fire is produced, even in oxygen gas. Tellurethyl treated with nitric acid, causes violent evolution of nitric oxide, and forms a solution from which aqueous hydrochloric acid throws down a heavy, colourless oil. — Tellurethyl is nearly insoluble in water. (Wöhler.)

¶. *Oxide of Tellurethyl.* — Not yet obtained in a state of purity, its isolation being always attended with partial decomposition. It may be obtained: 1. By direct oxidation of the alcoholic solution in the air; the process is however very slow and not adapted for a method of preparation. (Mallet.) — 2. By treating the chloride immersed in water with recently precipitated oxide of silver, which immediately acts upon it with spontaneous evolution of heat, and is converted into chloride. The filtered liquid is an aqueous solution of oxide of tellurethyl free from silver and chlorine. By evaporation at a gentle heat, the oxide is obtained as a white mass having a very distinct crystalline character. (Mallet.) — 3. Wöhler, by digesting a solution of the crystallized oxychloride with recently precipitated oxide of silver, found that chloride of silver was immediately formed; but the liquid did not filter well, the excess of oxide of silver running through. On evaporating it in the water-bath to a syrup, it began to smell of tellurethyl, and the undissolved matter turned black. On dilution with water, it filtered clearly; but the solution when again evaporated to a syrup, gave off an odour of tellurethyl and began suddenly to give off a gas (carbonic acid absorbed from the air) with effervescence. — 4. A solution of the sulphate was decomposed with a hot-saturated solution of baryta water, the excess of baryta removed by carbonic acid, the liquid heated some time to expel the carbonic acid, and then filtered. The solution, when evaporated over the water-bath, smelt constantly of tellurethyl, and, as soon as it was brought down to

the consistence of turpentine, gave off gas with effervescence. The same evolution of gas was subsequently produced in the cold mass by stirring it. The syrupy residue exhibited signs of crystallization. (Wöhler.)

The crystalline oxide obtained by Mallet decomposed when heated in a tube, yielding metallic tellurium and an oil having a very offensive odour. In the air it burned with the blue flame of tellurium. (Mallet.) — The solution of the oxide has an alkaline reaction, and when mixed with hydrochloric acid, yields chloride of tellurethyl in colourless oily drops. (Wöhler, Mallet.) — Yields a crystalline salt with nitric acid. (Wöhler.)

Sulphide. C^4H^5TeS. — Sulphuretted hydrogen passed through a solution of the nitrate throws down an orange-coloured precipitate, which on heating the liquid melts into black drops. (Mallet.)

Sulphate. $C^4H^5TeO,HO + C^4H^5TeO,SO^3$. — Obtained by adding a hot, neutral, saturated solution of sulphate of silver to a solution of oxychloride of tellurethyl, as long as any chloride of silver is formed. — Crystallizes in groups of small, short, colourless prisms, easily soluble in water. Sulphurous acid precipitates from its solution a yellow oily body, of a most disagreeable odour. Chloride of barium throws down sulphate of baryta and reproduces the oxychloride. The percentage of sulphuric acid found was 15·10; the above formula requires 15·91.

Iodide. — C^4H^5TeI. — Formed by mixing a solution of the nitrate, oxychloride or oxybromide with hydriodic acid, or by supersaturating the chloride with this acid. The iodide separates in the form of a very beautiful orange-coloured precipitate, which when washed and dried forms an orange-yellow powder. Heated in water it melts at 50°, to a heavy, yellowish red liquid, which, on cooling, solidifies to a yellowish red, opaque, scaly, crystalline mass, which like mica, may be very easily broken in the direction of the cleavage-plane. Dissolves sparingly in water, but readily in hot alcohol, from which it crystallizes in long, thin, orange-yellow prisms. When heated above its melting point, it decomposes, yielding a yellowish red oil, a black sublimate, and metallic tellurium. — If a partially decomposed solution of hydriodic acid be used in the preparation of this body, an almost blood-red precipitate is obtained, most probably containing a higher iodide.

5. *Oxyiodide.* C^4H^5TeO, C^4H^5TeI. — Obtained by dissolving the iodide in ammonia, and leaving the solution to evaporate spontaneously. Crystallizes readily as the ammonia volatilizes, in pale yellow transparent prisms, isomorphous with the corresponding chlorine and bromine compounds. These crystals become orange-yellow on the surface when exposed to the air. They are but sparingly soluble in pure water, but dissolve freely in water containing excess of ammonia. Hydrochloric acid added to the aqueous solution, throws down a heavy, yellowish red mixture of chloride and iodide of tellurethyl. Sulphuric acid throws down the orange-yellow iodide; and hydrochloric acid added to the filtrate separates the colourless chloride. Sulphurous acid precipitates from the solution of the oxyiodide, an easily fusible, semisolid mixture of tellurethyl and the iodide.

Bromide. C^4H^5TeBr. When a solution of the oxychloride or the

nitrate is mixed with hydrobromic acid, the bromide separates in the form of a pale yellow, very heavy, inodorous oil.

Oxybromide. C^4H^5TeO,C^4H^5TeBr. — Obtained by dissolving the bromide in ammonia. Crystallizes in shining, colourless prisms, of the same form as the corresponding chlorine-compound, to which it is perfectly analogous.

Chloride. C^4H^5TeCl. — Obtained by mixing a solution of the nitrate not containing a great excess of nitric acid, with strong hydrochloric acid in a narrow cylindrical vessel. The mixture becomes milky at first, but after a while the chloride sinks to the bottom in the form of a heavy oil. It may be washed with water, though it is somewhat soluble in that liquid, and also in strong hydrochloric acid. When the latter solution is evaporated at a gentle heat, the chloride separates in oily drops. (Wöhler, Mallet.) The chloride is also precipitated as an oil on adding hydrochloric or sulphuric acid to a solution of the sulphate or oxychloride. (Wöhler.)

Transparent and colourless oil, heavier than water, and having an unpleasant odour. May be distilled without decomposition, but appears to have a very high boiling point, for when distilled with water it passes over very slowly. — Oxide of silver decomposes this compound, converting it into oxide of tellurethyl. (Mallet, p. 384.)

				Mallet.
4 C	24·0	....	18·69	
5 H	5·0	....	3·90	
Te	64·0	....	49·84	50·55
Cl	35·4	....	27·57	27·07
C^4H^5TeCl	128·4	....	100·00	

Oxychloride. — C^4H^5TeO, C^4H^5TeCl. — Obtained by dissolving the chloride in caustic ammonia or potash, and evaporating the solution till it crystallizes. It is best to add ammonia, because an excess of it does not decompose the product. The salt crystallizes easily as the excess of ammonia evaporates. The mother-liquor contains sal-ammoniac or chloride of potassium:

$$2C^4H^5TeCl + KO = KCl + C^4H^5TeO,C^4H^5TeCl.$$

Colourless, highly lustrous, six-sided prisms, soluble in water and alcohol; a solution of the compound in hot alcohol yields very beautiful crystals.

				Wöhler.
8 C	48·0	....	20·89	19·94
10 H	10·0	....	4·36	4·96
2 Te	128·0	....	55·88	56·22
Cl	35·4	....	15·44	15·19
O	8·0	....	3·43	3·39
$C^8H^{10}Te^2ClO$	229·4	....	100·00	100·00

Hydrochloric acid added to solutions of this compound, throws down colourless oily chloride of tellurethyl, a small quantity of which remains in solution. Sulphuric acid also precipitates the chloride, while sulphate of tellurethyl remains in solution, and from this the chloride may be precipitated by hydrochloric acid. (Wöhler.)

Fluoride. — Hydrofluoric acid added to solutions of the oxychloride throws down chloride of tellurethyl, while a soluble fluorine-compound remains in solution and may be crystallized by evaporation. The same compound is obtained by treating free oxide of tellurethyl with hydrofluoric acid. (Wöhler.)

Nitrate. C^4H^5TeO,NO^5. — Obtained in the form of a white, crystalline mass by dissolving tellurethyl in moderately strong nitric acid, and evaporating to dryness at a gentle heat. — This salt burns away like gunpowder when heated. It dissolves readily in water. Alkalis added to the solution form no precipitate, because the oxide of tellurethyl is soluble in water. — Sulphurous acid separates tellurethyl in dark red drops. — Sulphuretted hydrogen throws down the sulphide (p. 385). Hydrochloric acid precipitates the chloride. (Mallet.)

Bitelluride of Ethyl or *Telluride of Tellurethyl*, $C^4H^5Te^2 = C^4H^5Te + Te$. — This compound was first obtained by Mallet in endeavouring to prepare telluric mercaptan by saturating an aqueous solution of telluride of potassium and sulphovinate of baryta with telluretted hydrogen, and distilling. At first nothing but tellurethyl passed over; but on applying a stronger heat, another liquid distilled over, having a much greater density and higher boiling point, and so deep a red colour, that even in small quantities it appeared black and opaque like bromine. It likewise possesses an extremely offensive odour. (Mallet.)

			Mallet.
4 C	24	15·29	
5 H	5	3·18	
2 Te	128	81·53	79·31
$C^4H^5Te^2$	157	100·00	

The same compound is obtained in small quantity in the preparation of tellurethyl by the method given on page 384. When about $\frac{5}{6}$ of the tellurethyl has passed over, a small quantity of the bitelluride likewise distils over, distinguished by its deep red colour. (Wöhler.) ¶.

Detonating Platinum-deposit. $C^4H^4Pt^2O^2$?

ZEISE (1830). *Pogg.* 21, 502. — *J. pr. Chem.* 20, 313.

Formation. Vid. pp. 247, 248.

Preparation. — 1. Precipitated when bichloride of platinum is boiled with 10 times its weight of alcohol, the quantity formed increasing with the amount of protochloride of platinum present; it is therefore obtained in the preparation of ethylo chloride of platinum (p. 389). The precipitate is washed with hot water, the first portions of which may contain potash, till it no longer yields chlorine, and then dried in vacuo. — 2. One part of protochloride of platinum prepared by heating the bichloride and still containing some of that compound, is shaken up with 8 pts. alcohol of sp. gr. 0·816; then distilled in a retort with about 4 pts. more alcohol, till about 4 pts. have passed over, and the residual liquid, having deposited a black powder which causes percussive ebullition, becomes first green and then yellow; the product is then washed and dried as in (1).

—3. Ethylochloride of platinum, or the compound which it forms with chloride of potassium, is dissolved in water and heated with caustic potash; a black precipitate then forms which must be washed and dried. Magnesia likewise throws down this black powder when the mixture is heated.

Properties. Black, scentless powder. Contains a few particles of metallic platinum, and consequently acquires metallic lustre here and there by friction.

Decompositions. — The powder, when heated, detonates with a certain degree of sparkling, but with less noise than fulminating gold, and leaves grey metallic platinum which becomes red-hot by contact with alcohol, but does not set the alcohol on fire. The powder prepared by (3) exhibits the strongest detonation, probably because it contains the smallest quantity of metallic platinum. — The powder thrown upon paper moistened with alcohol, soon produces a slight explosion, the alcohol generally taking fire. When hydrogen gas mixed with air is projected upon the powder, the hydrogen soon takes fire. The powder, when kept for a long time loses its power of detonating when heated, but retains that of setting fire to alcohol. — If the powder is not perfectly free from chlorine, which is the case when an insufficient quantity of alcohol has been used, or the boiling or the washing has not been continued long enough, it does not possess the power of setting fire to alcohol. — Moreover, it undergoes some change even during washing; for it constantly gives off air bubbles even when washed with thoroughly boiled water. (Zeise.)

Ethylo-chloride of Platinum. C^4H^4,Pt^2Cl^2.

ZEISE, *Pogg.* 21, 497 and 542; also *Schw.* 62, 393; 63, 121 and 136.—*Pogg.* 40, 234.

Inflammable, or detonating Chloride of Platinum, Hydrocarburetted Chloride of Platinum, Chlorplatin-Vine, entzündliches verpuffendes Chlorplatin, gekohlenwasserstoffes Chlorplatin [*Pletek-Vine*]. — Discovered and examined by Zeise in 1830.

Formation (pp. 247, 248).

Preparation. 1. One part of bichloride of platinum, as free as possible from protochloride, is dissolved in 10 pts. alcohol of sp. gr. 0·82; the solution distilled till the residue is brought down to $\frac{1}{6}$ (a very gentle heat being applied towards the end of the operation, because the mixture is very apt to jump and splash over); the liquid residue filtered to separate it from the black, inflammable platinum deposit; the filtrate (the *crude liquid*) cautiously evaporated to dryness; the brown residue, mixed with black and yellow particles, exhausted with cold water; and the yellowish brown solution separated from the undissolved brown gummy substance, and evaporated, — most advantageously in vacuo, because in that case there is not so much insoluble brown matter reproduced. The yellow or yellowish brown residue is then redissolved in water, a few brown particles again remaining undissolved, and the filtrate evaporated in vacuo over hydrate of potash: ethylochloride of platinum then remains in a state of tolerable purity. (Zeise.)

2. A concentrated aqueous solution of bichloride of platinum is added to a concentrated aqueous solution of the compound of ethylochloride of platinum and sal-ammoniac, as long as a precipitate of chloroplatinate of ammonium continues to fall; the liquid quickly filtered, and evaporated quickly in vacuo, first over oil of vitriol, and then over oil of vitriol and hydrate of potash; the gummy and friable residue washed with a small quantity of water to remove any excess of bichloride of platinum or of the compound of ethylochloride of platinum with sal-ammoniac that may be present; then dissolved in a larger quantity of lukewarm water, filtered from the chloroplatinate of ammonium, and evaporated in vacuo. This method yields the purest product. (Zeise.)

Properties. Very pale lemon-coloured substance. (Zeise.)

Calculation, from the analysis of the compound which it forms with Chloride of Potassium.

4 C	24·0	....	8·09
4 H	4·0	....	1·35
2 Pt	198·0	....	66·71
2 Cl	70·8	....	23·85
C^4H^4,Pt^2Cl^2	296·8	....	100·00

Decompositions. 1. Ethylochloride of platinum becomes brown and black by exposure to light. — 2. When subjected to dry distillation, it froths up moderately; gives off a large quantity of hydrochloric acid gas and carburetted hydrogen; and leaves a black residue, which, when heated in the air, burns without flame like charcoal, and leaves metallic platinum. — 3. If set on fire in the air before it has been ignited, it burns with flame and leaves white metallic platinum having a silvery lustre. — 4. The aqueous solution heated to the boiling point, quickly becomes turbid, and deposits nearly all the platinum in the metallic state, at the same time giving off hydrochloric acid and a large quantity of combustible gas, but neither alcohol nor ether. The solution likewise becomes decolorized and deposits a brown mucus, even at ordinary or slightly elevated temperatures, especially if exposed to light. The aqueous solution of the pure compound obtained by (2) may be evaporated in vacuo without decomposition; but the solution of the compound prepared by (1), suffers some degree of decomposition when thus evaporated. If however a large quantity of hydrochloric acid be added to the aqueous solution, it is not decomposed even by boiling. — 5. If nitrate of silver be added to the aqueous solution just so long as a precipitate of chloride of silver continues to form — which precipitate has a yellowish white colour and pulverulent character, arising from admixture of platinum-deposit — and the liquid be then filtered, the filtrate becomes turbid in a few minutes and soon yields a large quantity of platinum-deposit in the form of a black powder, which increases considerably on the application of heat, after which the filtrate will again throw down chloride of silver from a solution of the nitrate. Part of the chlorine is therefore more intimately combined than the rest. — The aqueous solution mixed with excess of potash yields, after a few days, a brown-grey gummy deposit, retaining however a considerable quantity of platinum which is not precipitated till the liquid is heated. If the aqueous solution be immediately heated with excess of potash, it gives off a gas and a distillate which smells like tallow, and deposits a black powder mixed with metallic scales, which when dried and then strongly heated, detonates with violence; it also sets

fire to alcohol. — The aqueous solution shaken up with magnesia also yields a brown-grey, gummy precipitate which subsequently changes to a black powder. This powder, if freed from magnesia by dilute nitric acid, then well washed and dried in vacuo, likewise explodes violently when heated. — 7. Copper immersed in the aqueous solution, forms chloride of copper, and throws down a black precipitate which detonates when heated. Mercury acts in a similar manner, but part of it unites with the platinum forming an amalgam. — 8. Sulphuretted hydrogen passed through the aqueous solution, eliminates a gas, decolorizes the liquid completely, and forms a yellow precipitate, which soon turns black, and if heated after being dried in vacuo, first gives off sulphur and sulphurous acid, and is then completely decomposed with a crackling noise and emission of sparks. The liquid filtered from the yellow, blackening precipitate contains nothing but hydrochloric acid and a small quantity of chloride of platinum. (Zeise.)

Combinations. — Inflammable chloride of platinum does not become moist when exposed to the air, and dissolves but slowly in *water*, forming a yellow solution. (Zeise.)

Ethylochloride of Platinum with Ammonia. — Obtained by precipitating a concentrated aqueous solution of ethylochloride of platinum, or its compound with sal-ammoniac or chloride of potassium, with a slight excess of caustic ammonia or carbonate of ammonia. If the compound with chloride of potassium be used, that salt is found in the filtrate. With the sal-ammoniac compound, potash may be used for the preparation instead of ammonia. Caustic ammonia in large excess exerts a decomposing action on the compound; hence it is better to use carbonate of ammonia. (Zeise.)

The bulky, and at first light-yellow precipitate blackens by exposure to air and light; its colour is also gradually changed by the action of water or alcohol. — When subjected to dry distillation, it gives off a combustible gas, hydrochloric acid gas, and sal-ammoniac, and leaves a mixture of platinum and charcoal. As it burns in the air, the mass finally takes fire from end to end. The compound dissolves in water somewhat more readily than gypsum; the solution treated with potash gives off ammonia, and when heated with an acid, deposits metallic platinum. Alcohol appears to dissolve the compound more readily than water. Dilute hydrochloric acid colours it a darker yellow, and then dissolves it, producing the following compound. (Zeise.)

Dried in vacuo, then at 100°.			Zeise.
NH^3	17·0	5·42	
4 C	24·0	7·65	
4 H	4·0	1·27	
2 Pt	198·0	63·10	62·45
2 Cl	70·8	22·56	22·63
$NH^3 + C^4H^4Pt^2Cl^2$	313·8	100·00	

Ethylochloride of Platinum with Sal-ammoniac. — *Inflammable Chloroplatinate of Ammonium.* — The *crude liquid* (p. 388), which should not be rendered turbid by a concentrated solution of chloride of potassium, is diluted with a fourfold quantity of water, and decanted from the detonating platinum deposit; a quantity of sal-ammoniac, amounting to 18 per cent. of the bichloride of platinum used to form the crude liquid, is then dissolved in it; the solution evaporated down to one-third; the brown crystalline

mass which forms on cooling broken up, and dissolved in a small quantity of warm water, after the very acid mother-liquid has run off; the solution evaporated at a gentle heat and cooled to the crystallizing point; and the crystals washed with a small quantity of water, then dissolved in a larger quantity, and the solution left to crystallize by evaporation in vacuo. In this stage of the operation, heat would exert a decomposing action, because the solution no longer contains hydrochloric acid.

Lemon-yellow, transparent, shining, oblique rhombic prisms, often half an inch long, which become covered with a black film by exposure to air and light. (Zeise.)

	Dehydrated.			Zeise.
N	14·0	....	4·00	
4 C	24·0	....	6·86	
8 H	8·0	....	2·28	
2 Pt	198·0	....	56·54	56·16
3 Cl	106·2	....	30·32	30·02
$NH^4Cl + C^4H^4,Pt^2Cl^2$	350·2	....	100·00	

The cyrstals contain 6·18 per cent. ($2\frac{1}{2}$, or perhaps more correctly 2 At.) water of crystallization, which they give off at 100° or in vacuo without further decomposition; heated to redness in the air, they leave platinum. Their aqueous solution, when heated alone, or mixed either hot or cold with excess of potash, exhibits the same decompositions as the solution of ethylochloride of platinum heated alone. Mixed with caustic potash and evaporated, it yields a white precipitate. Bichloride of platinum precipitates the sal-ammoniac in the form of chloroplatinate of ammonium. The crystals dissolve in less than 5 pts. of cold water, more sparingly in alcohol. (Zeise.)

Ethylochloride of Platinum with Chloride of Potassium. — Inflammable Platinopotassic Salt. — Obtained by diluting the crude liquid in the retort (p. 388) with about four times its bulk of water; decanting it from the detonating platinum-deposit; dissolving in it a quantity of chloride of potassium equal to $\frac{1}{4}$ of the bichloride of platinum used for the preparation of the crude liquid; and otherwise proceeding as in the preparation of the sal-ammoniac compound.

Large, lemon-yellow, transparent, shining, oblique rhombic prisms, u'; $u = 103° 58'$; *oblique terminal face* : $u = 112° 5'$. (Forchhammer.) Reddens litmus. Has a persistently astringent and metallic taste. (Zeise.)

	Dehydrated.			Zeise.
K	39·2	....	10·56	10·61
4 C	24·0	....	6·46	6·40
4 H	4·0	....	1·07	1·07
2 Pt	198·0	....	53·31	52·92
3 Cl	106·2	....	28·60	28·64
$KCl + C^4H^4,Pt^2Cl^2$	371·4	....	100·00	99·64

Liebig (*Pogg.* 31, 329, and *Ann. Pharm.* 23, 12) formerly assigned to this salt the formula: KCl,C^4H^5O,Pt^2Cl^2, according to which it would contain ether instead of ethylene, — and more recently the formula: $KCl,C^4H^3Pt^2Cl^2 = KCl,C^4H^3Cl,Pt^2Cl$. But the repeated analyses made by Zeise are more in favour of his own formula, $KCl,C^4H^4Pt^2Cl^2$. Malaguti's formula (*Ann. Chim. Phys.* 70, 403), viz. KCl,C^4H^3O,Pt^2Cl^2, is altogether improbable, inasmuch as the analysis and the reactions of the salt show that it does not contain oxygen.

The crystallized salt exposed to light and air becomes covered with a black crust. It contains 4·72 p. c. (2 At.) water of crystallization, which it gives off completely between 100° and 150° in a current of dry air; it likewise effloresces at ordinary temperatures in very dry air, and quickly in vacuo. The dry salt blackens at about 200°; gives off without any tumefaction a mixture of 2 vol. hydrochloric acid gas, and 1 vol. combustible gas; and leaves a grey mass likewise containing chloroplatinate of potassium. The escape of gas ceases before the mass becomes red-hot; the substance does not exhibit any glow; and no odour of ether is perceptible unless the salt has not been well dried. Chlorine gas acts on the dry salt only when aided by heat; it then forms hydrochloric acid and sesquichloride of carbon. Chlorine, bromine, and iodine added to the aqueous solution of the salt, emit an odour of ether. The dry pulverized salt heated in a stream of hydrogen gas, blackens and exhibits traces of moisture, but does not undergo complete decomposition till it is heated in the current of gas. A stream of hydrogen passed through the aqueous solution gradually throws down the greater part of the platinum in the metallic state. The aqueous solution of the chloride of potassium salt exhibits, when treated with nitrate of silver, the same reaction as ethylochloride of platinum alone. With ammonia, it quickly yields a yellow precipitate of the compound of ethylochloride of platinum with ammonia. When mixed cold with solution of caustic potash, it loses nearly all its colour, and deposits a brown gummy mass; when heated with it immediately, it behaves like a solution of ethylochloride of platinum. The solution decomposes at a gentle heat somewhat less quickly than that of ethylochloride of platinum; at 90° it exhibits rapid decomposition, but a certain quantity of platinum always remains in solution. In this case also hydrochloric acid, as well sulphuric and nitric acid, prevents the decomposition, even at a boiling heat; an excess of chloride of potassium appears also to exert a protecting action.

The compound of ethylochloride of platinum with chloride of potassium dissolves in 5 pts. of moderately warm water, forming a yellow solution, and less copiously in alcohol. (Zeise.)

Ethylochloride of Platinum with Chloride of Sodium. — Difficult to crystallize, dissolves somewhat slowly in alcohol, forming a yellow solution, unless an acid is present.

Does *Chloride of Rhodium* form a similar compound? *Comp.* Biewend (*J. pr. Chem.* 15, 128.)

Copulated Compounds of the Primary Nucleus, C^4H^4.

Carbonate of Ethyl. $C^6H^5O^3 = C^4H^5O,CO^2 = 2C^4H^5O,C^2O^4$.

Ettling. *Ann. Pharm.* 19, 17; also *Pogg.* 39, 157.
Cahours. *N. Ann. Chim. Phys.* 9, 201; also *Ann. Pharm.* 47, 291; also *J. pr. Chem.* 30, 241.

Carbonic Ether, Ethylic Carbonate, Kohlensaures Aethyloxyd, Kohlen-Vinester, Ether carbonique.—Discovered by Ettling in 1836.

Preparation. 1. Oxalic ether free from water and oil of wine is heated in a retort with sodium to 130°, and fresh sodium added as long as it causes any evolution of carbonic acid gas. The resulting dark red thickish mass is dissolved in water, and the carbonic ether which rises to the top of the aqueous solution is washed with water and distilled with a fresh quantity of water; then, if it still contains oxalic ether, it is dried over chloride of calcium, rectified over a small quantity of sodium, and — as the soda may have given rise to the formation of alcohol — heated alone in a retort till the boiling point becomes stationary, the portions which afterwards pass over being collected in a separate receiver. (Ettling.) — Potassium acts in a similar manner. (Cahours.) — Respecting the mode of formation, *vid. Decompositions of Oxalic ether.*

Properties. Thin, transparent, and colourless liquid of sp. gr. 0·975 at 19°. (Ettling.) Lighter than water. (Cahours.) Boils from 125° to 126° (Ettling); at 125° (Cahours.) Vapour-density 4·243 (Ettling); 4·09 (Cahours.) Odour, refreshing (Ettling), sweet and ethereal (Cahours); taste, burning and aromatic.

			Ettling.	Cahours.		Vol.	Density.
5 C	30	50·85	50·95	50·72	C-vapour	5	2·0800
5 H	5	8·47	8·53	8·67	H-gas	5	0·3465
3 O	24	40·68	40·52	40·61	O-gas	1½	1·6639
$C^5H^5O^3$	59	100·00	100·00	100·00	Carb. ether vapour	1	4·0904

If the formula be $C^5H^5O^3$, the vapour is monatomic; but if the true formula be $C^{10}H^{10}O^6$, the vapour is diatomic.

Decompositions. 1. Carbonic ether burns on a glass rod with a small blue flame. (Ettling.) — 2. Chlorine gas passed through it in daylight is absorbed, with rise of temperature and evolution of a large quantity of hydrochloric acid gas; and if the passage of the gas be continued for some time, the ether is ultimately converted at 70° or 80°, into bichlorinated carbonic ether, $C^4Cl^2H^3O,CO^2$; and this, if chlorine be passed through it for a still longer time in sunshine, is transformed into crystalline perchlorinated carbonic ether, C^4Cl^5O,CO^2. (Regnault.) — 3. The mixture of carbonic ether with alcoholic potash becomes turbid when heated, and deposits carbonate of potash; the supernatant liquid contains neither oxalic nor formic acid. (Ettling.) — 4. Sodium does not act upon carbonic ether in the cold, but when heated with it, eliminates carbonic oxide, and forms a white saline mass consisting of ethylate of sodium [$C^4H^5NaO^2$], and carbonate of soda [?]. (Löwig, *Pogg.* 50, 122). Probably in this manner:

$$C^5H^5O^3 + Na = C^4H^5NaO^2 + CO.$$

Carbonic ether is not soluble in water, but dissolves readily in common ether and in alcohol. (Cahours.)

¶ *Ethylo-methylic Carbonate.* — $C^2H^3O,C^4H^5O,2CO^2$. — Formed by distilling 1 At. carbomethylate of potassium (VII, 290) with 1 At. sulphovinate of potassium (Chancel, *Compt. rend.* 31, 521):

$$KO,C^2H^3O,2CO^2 + KO,C^4H^5O,2SO^3 = 2(KO,SO^3) + C^2H^3O,C^4H^5O,2CO^2.$$

No details respecting this compound have yet been published. ¶

Carbovinic Acid. $C^4H^5O^2,2CO^2 = HO,CO^2 + C^4H^5O,CO^2$.

DUMAS & PÉLIGOT (1840). *Ann. Chim. Phys.* 74, 9; also *Ann. Pharm.* 35, 284; also *J. pr. Chem.* 13, 372.

Weinkohlensaure, Aetherkohlensäure. Acide carbovinique. — Known only in the form of a potash-salt.

Preparation of the Potash-salt. — Hydrate of potash previously freed from excess of water by ignition, is dissolved in absolute alcohol, and carbonic acid gas passed through it in such a manner as to avoid all evolution of heat which might arise from the absorption; for this purpose, it is best to introduce from time to time portions of anhydrous ether or lumps of solid carbonic acid. As soon as an abundant crystalline precipitate of monocarbonate and bicarbonate, together with carbovinate of potash, is formed, the liquid is mixed with an equal volume of ether; the precipitate collected on a filter; shaken up with absolute alcohol, which dissolves only the carbovinate of potash; that salt precipitated, after filtration, by the addition of ether, then collected on a filter, and quickly dried.

Crystalline, with a pearly lustre.

			Dumas & Péligot.
KO,CO^2	69·2	53·98	53·47
5 C	30·0	23·40	23·37
5 H	5·0	3·90	3·98
3 O	24·0	18·72	19·18
$C^2H^5KO^2,2CO^2$	128·2	100·00	100·00

$= KO,CO^2 + C^4H^5O,CO^2$.

This salt, when subjected to dry distillation, yields a combustible gas, a small quantity of ethereal liquid, and a mixture of carbonic acid and charcoal. It burns on platinum foil with flame, leaving a carbonaceous residue. It decomposes in contact with water (less quickly with aqueous alcohol), yielding alcohol and a crystalline precipitate of bicarbonate of potash (Dumas & Péligot):

$$C^4H^5KO^2,2CO^2 = C^4H^6O^2 + KO,2CO^2.$$

Terbasic Borate of Ethyl. $3C^4H^5O,BO^3$.

EBELMEN & BOUQUET. *N. Ann. Chim. Phys.* 17, 55; also *J. pr. Chem.* 38, 215; abstr. *Compt. rend.* 22, 366; abstr. *J. pr. Chem.* 38, 215.
BOWMAN. *Phil. Mag. J.* 29, 546; also *Mem. and Proc. of the Chem. Soc.* 3, 248.

Drittel Borvinester, Einfach [?] borsaures Aethyloxyd, Protoborate éthylique, Terbasic Boracic Ether. — Discovered by Ebelmen & Bouquet in 1846.

Preparation. Chlorine gas is passed through a red-hot mixture of boracic acid and charcoal, and the resulting mixture of chloride of boron and carbonic oxide gas (II, 327), condensed in a bottle containing absolute alcohol and surrounded with cold water, the process being continued

so long as there is no risk of an admixture of free chlorine with the gas which comes over. Hydrochloric acid vapours are then evolved, and above the yellow alcohol saturated with hydrochloric acid, there is formed a rapidly increasing layer of the compound ether:

$$3C^4H^6O^2 + BCl^3 = 3C^4H^5O,BO^3 + 3HCl.$$

This liquid is decanted and distilled with a few drops of alcohol. At first a small quantity of alcohol containing hydrochloric acid passes over; then between 115° and 125° the boracic ether, which must be collected in a separate receiver. In the retort there remains a colourless, inflammable, vitreous mass, which solidifies on cooling, tastes very bitter, smells like terbasic boracic ether, but is not so readily decomposed by water; it contains 20·7 p. c. carbon and 6·0 H, (may, therefore, be $2C^4H^5O,3BO^3$.)—By rectifying the distillate, so that all which passes over at 119° may be collected apart, the boracic ether is obtained in a state of purity. (Ebelmen & Bouquet.) — Bowman proceeds in a similar manner, excepting that he first passes the mixture of chloride of boron and carbonic oxide through a U-tube filled with copper-filings, to remove all the free chlorine, and then into the absolute alcohol contained in a Liebig's bulb-apparatus immersed in cold water. In conducting the experiment in this manner, it is observed that a heavy liquid first forms, with evolution of heat, in the first bulb, then sinks down and forms a clear mixture with the remaining alcohol, — and that the alcohol afterwards becomes turbid, without evolution of heat, the turbidity arising from the separation of small drops of liquid, which unite and rise as a layer of the compound ether to the top of the heavier stratum. The boracic ether is then decanted and fractionally distilled four times to free it from the adhering acid layer, which is heavier but more volatile; in the first distillation, vapours of hydrochloric acid and chloride of ethyl are evolved. The heavy acid stratum has a density of 0·901, boils at about 88°, giving off hydrochloric acid and chloride of ethyl, and contains 46·29 per cent. of carbon, 11·56 hydrogen, 9·53 chlorine, and 32·52 oxygen, together with a trace of carbonic acid, [appears, therefore, to be a mixture of alcohol and hydrochloric acid.] (Bowman).

Properties. Transparent, colourless, very thin liquid, of sp. gr. 0·8849 at 0° (Ebelmen & Bouquet); 0·871 (Bowman). Boils at 119°, according to Ebelmen & Bouquet; at 121°, according to Bowman. Vapour-density, 5·14 (Ebelm. & B.); 5·31 (Bowman); has a peculiar and tolerably agreeable odour; tastes warm and bitter (Ebelm. & Bouquet); has a pungent aromatic odour and a sharp taste. (Bowman.)

			Ebelm. & B.	Bowman.
12 C	72·0	49·38	49·12	47·69
15 H	15·0	10·29	10·43	9·90
3 O	24·0	16·46	18·05	17·94
BO^3	34·8	23·87	22·40	24·29
Cl				0·18
$3C^4H^5O,BO^3$	145·8	100·00	100·00	100·00

	Vol.	Density.
C-vapour	12	4·9920
H-gas	15	1·0395
B-vapour	1	0·7487
O-gas	3	3·3279
Vapour of $3C^4H^5O,BO^3$	2	10·1081
	1	5·0540

Decompositions. Terbasic boracic ether burns with a beautiful green flame, giving off white fumes of boracic acid and leaving no residue. (Ebelm. & B.); according to Bowman, it leaves a residue of fused boracic acid. — It dissolves quickly in water, decomposing at the same time into alcohol and boracic acid which settles at the bottom; it is decomposed in the same manner by moist air. (Ebelm. & Bouquet.) Hence, when exposed to moist air, it reddens litmus paper. The boracic ether separated by a small quantity of water disappears on the addition of a larger quantity. Aqueous ammonia or potash likewise decomposes the ether, yielding alcohol and a borate of the alkali. (Bowman.) — Distilled with alcohol of 36° Bm. it passes over for the most part undecomposed, leaving only a very small quantity of boracic acid. (Ebelm. & Bouquet.)

It mixes in all proportions with *Alcohol* and *Vinic ether*. (Ebelmen & Bouquet, Bowman.)

Biborate of Ethyl. $C^4H^5O,2BO^3$.

EBELMEN (1844). *N. Ann. Chim. Phys.* 16, 129; also *Ann. Pharm.* 57, 319; also *J. pr. Chem.* 37, 348; abst. *Compt. rend.* 18, 1202.

Doppelt-Borvinester, Zweifach-boraxsaures Aethyloxyd, Biborate éthylique.

Vitrefied boracic acid in the state of fine powder becomes heated from 18° to 50° when mixed with an equal weight of absolute alcohol; at 95°, the mixture begins to boil. As soon as the boiling point has risen to 110°, the distillation is interrupted; the portion which has distilled over poured back; the distillation repeated till the boiling point again rises to 110°; the half solid residue broken into small pieces and digested for 24 hours with anhydrous ether; the liquid decanted from the undissolved portion; and distilled till the heat in the retort rises to 200°.

Biborate of ethyl then remains in the retort in the form of a thick yellowish liquid, which at 200° gives off white fumes in the air, and on cooling solidifies to a transparent glass. This glass is rather soft, even at ordinary temperatures, and at 40° or 50° may be drawn out into long threads. It has a faintly ethereal odour, a burning taste, and when placed on the skin produces a burn, being at the same time converted into a white powder of hydrated boracic acid.

			Ebelmen.
4 C	24·0	22·51	19·8
5 H	5·0	4·69	4·4
O	8·0	7·51	9·1
2 BO^3	69·6	65·29	66·7
$C^4H^5O,2BO^3$	106·6	100·00	100·0

Corresponds to hydrated boracic acid, $HO,2BO^3$, and borax $NaO,2BO^3$.

Begins to decompose at 300°, with fusion, intumescence, and thickening, the products being olefiant gas, alcohol vapour, vapour of undecomposed ethylic biborate, vapour of water, and fused boracic acid free from charcoal. At first the olefiant gas predominates, afterwards the alcohol vapour; lastly, water and hydrated boracic acid. [The last-mentioned

product is probably formed by the decomposition of the volatilized boracic ether, caused by the water which is given off towards the end of the process.] The olefiant gas evolved in the decomposition burns with a green flame, the colour arising from admixture of the vapour of the boracic ether, which, however, may be removed by washing with water. — Biborate of ethyl triturated with water becomes very hot, and is resolved into alcohol and boracic acid. When exposed to moist air, it becomes white on the surface from slow decomposition.

Biborate of ethyl dissolves in *Alcohol* and *Vinic ether*, but gives off these liquids completely at 200°; a portion of the undecomposed boracic ether then passes over with the alcohol, so that the distillate burns with a green flame, and when mixed with water, solidifies from separation of boracic acid. (Ebelmen.)

Ethylo-phosphorous Acid. $HO,C^4H^6O^2,PO^3=HO,C^4H^5O,PHO^4$

WURTZ (1845). *N. Ann. Chim., Phys.* 16, 218; abstr. *Comp. rend.* 21, 357.

Weinphosphorige Säure, Aetherphosphorige Säure, Acide étherophosphoreux.

Terchloride of phosphorus mixed with alcohol of 36° Bm. evolves great heat, and forms hydrochloric acid, ethylophosphorous acid, and chloride of ethyl:

$$PCl^3 + 2C^4H^6O^2 + 2HO = HO,C^4H^6O^2,PO^3 + C^4H^5Cl + 2HCl.$$

If absolute alcohol were used, there would be a deficiency of 2HO. A small portion of the phosphorous acid remains in the mixture in the free state. — The terchloride of phosphorus is added drop by drop to the alcohol in a vessel kept continually cold from without, and the mixture evaporated at a gentle heat to drive off the chloride of ethyl and the hydrochloric acid, first in the air, and afterwards in vacuo, the vessel containing the liquid being connected with the air-pump by a tube containing hydrate of potash. The remaining syrup is then saturated with carbonate of baryta, and separated by filtration from phosphite of baryta; the filtrate evaporated in vacuo; the dry residue treated with absolute alcohol; the liquid filtered to separate the chloride of barium, and evaporated till the baryta-salt crystallizes.

The acid itself is scarcely known in the free state, in consequence of its great tendency to resolve itself into phosphorous acid and alcohol.

Its salts, the *Ethylophosphites*, are more permanent than the acid, less disposed to crystallize, and readily soluble in water.

Potash-salt. — By precipitating the aqueous solution of the baryta-salt with sulphate of potash and evaporating the filtrate in vacuo, a thick, non-crystallizable syrup is obtained.

Baryta-salt. — White, amorphous, friable, and deliquescent mass having the composition: $HO,C^4H^5BaO^2,PO^3 = BaO,C^4H^6O^2,PO^3 = BaO,C^4H^5O,PHO^4$. This salt swells up when subjected to dry distillation, giving off, first certain volatile products of the decomposition of alcohol, then phosphuretted hydrogen gas, and leaving a mixture of phosphate of

baryta and oxide of phosphorus. In the dry state, it is permanent in the air; but in solution, it gradually deposits crystals of monophosphate of baryta, whilst alcohol makes its appearance in the acid liquid:

$$C^4H^6O^6BaP + 2O = C^4H^6O^2 + BaO,PO^5.$$

The salt dissolves very readily in water and alcohol; from the latter solution it is precipitated by ether.

Lead-salt. — Formed by saturating the acid separated by sulphuric acid from the baryta-salt, with recently precipitated carbonate of lead, and evaporating the filtrate in vacuo. Shining, unctuous, crystalline scales, permanent in the air, soluble in water and alcohol, insoluble in ether. The aqueous solution gradually deposits phosphite of lead.

	Crystallized.		Wurtz.
4 C	24·0	11·25	11·25
6 H	6·0	2·81	2·84
Pb	104·0	48·74	48·32
P	31·4	14·71	14·85
6 O	48·0	22·49	22·74
$PbO,C^4H^6O^2,PO^3$	213·4	100·00	100·00

Copper-salt. — Obtained by precipitating the baryta-salt with sulphate of copper, and evaporating the filtrate in vacuo. Blue, amorphous, soft, deliquescent mass, in which the copper is gradually reduced. (Wartz.)

¶ Phosphate of Ethyl. $3C^4H^5O,PO^5$.

VÖGELI. *Pogg.* 75, 282; abstr. *Ann. Pharm.* 69, 180; *J. pr. Chem.* 46, 157; *Pharm. Centr.* 1849, 129.

Ethylic Phosphate, Phosphorsaures Aethyloxyd, Phosphoric ether.

This body is obtained: 1. By the action of anhydrous phosphoric acid on alcohol, which, however, yields it in small quantity only.— 2. In the decomposition of biethylophosphates (p. 402) by heat. When biethylophosphate of lead is heated in an oil-bath to 180° — 190°, phosphoric ether is obtained in the form of a transparent and colourless liquid, which may be dried over recently ignited carbonate of potash and further purified by redistillation. The decomposition by which it is obtained is represented by the following equation:

$$2(\underbrace{PbO,2C^4H^5O,PO^5}_{\text{Biethylophosphate of lead.}}) = \underbrace{3C^4H^5O,PO^5}_{\text{Phosphoric ether.}} + \underbrace{2PbO,C^4H^5O,PO^5}_{\text{Phosphovinate of lead.}}.$$

The distillate does not taste sour, but faint and nauseating; it does not change the colour of litmus paper. Mixes with ether and alcohol, and even with water, although a drop of it placed upon glass repels water, a phenomenon likewise observed with alcohol.

The ether was not obtained perfectly anhydrous, and consequently its analysis exhibits a deficiency in the carbon and phosphoric acid. The highest boiling point observed (by passing the ether to the top of a tube filled with mercury and observing the temperature at which the tension of its vapour just balanced the atmospheric pressure) was 142° 5′.

					Vögeli.
12 C	72·0	....	39·47	.....	38·31
15 H	15·0	....	8·22	.....	8·59
3 O	24·0	....	13·16	.....	15·02
PO^5	71·4	....	39·15	.....	38·08
$3C^4H^5O,PO^5$	182·4	....	100·00	.....	100·00 ¶

Ethylophosphoric or Phosphovinic Acid

$HO,C^4H^6O^2,PO^5 = 2HO,C^4H^5O,PO^5$.

LASSAIGNE. *Ann. Chim. Phys.* 13, 294; also *Schw.* 29, 201; also *N. Tr.* 5, 1, 137.
PELOUZE. *Ann. Chim. Phys.* 52, 37; also *J. Chem. méd.* 9, 129; also *Schw.* 67, 330 and 355, *Ann. Pharm.* 6, 129.
LIEBIG. *Ann. Pharm.* 6, 149.

Phosphethylic acid, Aetherphosphorsäure, Weinphosphorsäure, Acide phosphovinique. — Discovered by Lassaigne in 1820, more minutely examined by Pelouze and Liebig.

For its formation from alcohol, *vid.* page 242. It is also formed by the action of phosphoric acid upon ether; but much more slowly than with alcohol. (Pelouze.)

Preparation. 1 pt. of 95 per cent. alcohol is mixed with 1 pt. of ordinary phosphoric or pyrophosphoric acid of the thickness of a strong syrup; the mixture heated for some minutes to 60° or 80°; diluted after 24 hours with 8 times its bulk of water, and neutralized with carbonate of baryta pulverized as finely as possible. The whole is then boiled for a while to drive off the uncombined alcohol, — then left to cool down to 70° — filtered — and the filtrate left in a cold place, so that the phosphovinate of baryta may crystallize out. From the aqueous solution of this salt, the acid may be obtained by carefully adding sulphuric acid, and filtering; it may also be obtained by decomposing the lead-salt with sulphuretted hydrogen, and filtering. Either of these filtrates evaporated, first over the open fire, and then over oil of vitriol in vacuo at ordinary temperatures, leaves the concentrated acid in the form of an oil which neither dries up nor decomposes when left for a longer time in vacuo. (Pelouze.)

The concentrated acid is a colourless, inodorous, viscid oil, which reddens litmus strongly, and has a biting sour taste. It deposits a few shining crystals of the acid, which, however, do not increase at 22°. When boiled, it first gives off ether mixed with alcohol, then olefiant gas with a trace of wine-oil, and leaves phosphoric acid mixed with charcoal. (Pelouze.) When distilled with acetate of potash, it yields pure acetic ether. (Liebig, *Ann. Pharm.* 13, 32.)

The concentrated acid mixes with water in all proportions, and may be concentrated by boiling up to a certain point without decomposition. (Pelouze.)

The *Phosphovinates, Ethylophosphates,* or *Phosphethylates,* contain 2 At. metal to 1 At. acid, and, according to Liebig's analysis of the baryta-salt, their composition is expressed by one of the following

formulæ: $MO,C^4H^5MO^2,PO^5$, or $HO,C^4H^4M^2O^2,PO^5$, or $C^4H^4M^2O^4,PHO^6$ (Gerhardt), or $2MO,C^4H^6O,PO^5$ (radical-theory). They sustain a heat of 200° without decomposition; some of them dissolve, though slowly, in water; but they dissolve readily in dilute acids. (Pelouze.)

Phosphovinate of Potash. — Obtained by precipitating the baryta-salt with sulphate of potash. Crystallizes very slowly and indistinctly; melts in its water of crystallization when heated, and is very deliquescent. (Pelouze.)

Phosphovinate of Soda. — Obtained in a similar manner, and similarly constituted.

Phosphovinate of Baryta. — Colourless, very short, right rhombic prisms, passing into six-sided tables by truncation of the acute lateral edges. Tastes agreeably saline and bitter. Effloresces very slowly in the air; gives off 30·575 per cent. (29·15 p. c. according to Liebig) of its water of crystallization at 120°, acquiring at the same time a pearly lustre. At a dull red heat, it gives off water and carburetted hydrogen, with traces of alcohol and ether, and leaves dipyrophosphate of baryta ($2BaO,PO^5$) mixed with charcoal. If the dry salt be mixed, before ignition, with carbonate of potash, it likewise yields no alcohol, but the same volatile products as when heated alone. (Pelouze.) The salt carefully dried and then heated till it chars, gives off olefiant gas and alcohol. (Liebig.) From the aqueous solution mixed at the ordinary temperature with nitric acid, alcohol throws down nitrate of baryta, while free phosphovinic acid remains in solution. The salt is most soluble in water at 40°, and the solution saturated at that temperature, deposits crystals of the 12-hydrated salt, both when heated and when cooled. 1 pt. of the (crystallized?) salt dissolves at 0° in 29·4 pts., at 5° in 30·3, at 20° in 14·9, at 40° in 10·7, at 50° in 12·5, at 55° in 11·2, at 60° in 12·4, at 80° in 22·3, and at 100° in 35·7 pts. of water. The salt is insoluble in alcohol and ether and is precipitated by these liquids from its aqueous solution. (Pelouze.)

Dried at 120°.			Pelouze.	Liebig.
2 BaO	153·2	58·56	56·90	85·92
PO^5	71·4	27·29	25·90	
4 C	24·0	9·18	9·17	9·28
5 H	5·0	1·91	2·26	1·69
O	8·0	3·06	5·77	3·11
$BaO,C^4H^5BaO^2,PO^5$	261·6	100·00	100·00	100·00

Crystallized.			Liebig.	Pelouze.
2 BaO	153·2	41·45	60·88	
PO^5	71·4	19·32		
4 C	24·0	6·49	6·58	
5 H	5·0	1·35	1·19	
O	8·0	2·17	2·20	
12 Aq.	108·0	29·22	29·15	30·575
$BaO,C^4H^5BaO^2,PO^5+12Aq.$	369·6	100·00	100·00	

According to Pelouze, the dry salt contains $2BaO,C^4H^6O^2,PO^5$.

Ethylophosphate of Strontia. — Crystallizes with difficulty in hydrated crystals; is much less soluble in hot water than in cold; and is precipitated from the cold solution by alcohol.

Phosphovinate of Lime. — Alcohol is added by drops, as in Boullay's process (p. 174), to an equal weight of phosphoric acid of sp. gr. 1·50, heated in a retort, the mixture distilled, and the distillate frequently poured back till it becomes rich in ether; the brownish viscid residue dissolved in water, supersaturated with milk of lime, and filtered from the phosphate of lime; carbonic acid gas passed through the filtrate to precipitate the free lime; and the liquid heated to the boiling point, then filtered and evaporated. Phosphovinate of lime then remains in the form of a white mass, consisting of fine needles and having a slightly sharp taste. When subjected to destructive distillation, it gives off a gas having the odour of acetic ether, together with water, oil of wine, and a mixture of charcoal and phosphate of lime. It also leaves this salt when mixed with nitric acid and evaporated. Dissolves readily in water, and when exposed to the air, becomes moist but does not deliquesce. (Lassaigne.)

Small micaceous needles having a strong lustre; precipitated on mixing the baryta-salt with nitrate or hydrochlorate of lime. They contain 4 At. water, dissolve slowly in pure water, but readily in water containing phosphovinic or acetic acid. (Pelouze.)

Ethylophosphate of baryta forms with *Protochloride of tin*, and with *Lead, Mercury*, and *Silver-salts*, precipitates which are soluble in dilute acids; but it forms no precipitate with protochloride or sesquichloride of iron, chloride of nickel, chloride of copper, terchloride of gold, or bichloride of platinum. (Pelouze.)

The dilute acid dissolves *Zinc* and *Iron* with evolution of hydrogen, forming a zinc or iron salt. (Pelouze.)

Phosphovinate of Lead. — Precipitated in the anhydrous state by adding phosphovinate of baryta to a lead-salt. It is the least soluble of all the phosphovinates.

				Pelouze.
2 PbO	224·0	67·39		86·28
PO^5	71·4	21·48		
4 C	24·0	7·22		7·68
5 H	5·0	1·50		1·81
O	8·0	2·41		4·23
$PbO,C^4H^5PbO^2,PO^5$	332·4	100·00		100·00

Phosphovinate of Silver. — The baryta-salt mixed with nitrate of silver throws down hydrated crystals, which resemble the lime-salt in appearance and in their slight solubility. (Pelouze.)

The concentrated acid mixes in all proportions with *Alcohol* and *Ether;* it coagulates white of egg. (Pelouze.)

¶ Biethylophosphoric Acid. $HO,2C^4H^5O,PO^5$.

VÖGELI. *Vid.* Memoir cited on page 398.

This acid is formed, together with the preceding, when absolute alcohol or ether, in the liquid or gaseous state, is brought in contact with anhydrous phosphoric acid. The absorption of the vapour affords the best mode of preparation, because when anhydrous phosphoric is introduced into liquid alcohol or ether, great heat is evolved, and the phosphoric acid forms into lumps, which are very slowly acted upon.

Preparation. Anhydrous phosphoric acid is placed over anhydrous ether or alcohol (the latter yields the best product), and the whole covered with a bell-jar to keep out the moisture of the air. — The acid then absorbs the vapour, and in a week or a fortnight deliquesces to a syrup. [In one experiment the acid absorbed about one-third of its weight of ether-vapour.] This syrup is saturated with carbonate of lead, the insoluble phosphate of lead, &c., removed by filtration, and the filtrate evaporated over a water-bath or a sand-bath. A sparingly soluble lead-salt (phosphovinate) then separates out in pearly crystals. On further concentration, the solution yields groups of crystals like theïn. These crystals consist of the biethylophosphate of lead; they may be purified by redissolving them at a very gentle heat and recrystallizing. — From the solution of this lead-salt the lead may be precipitated by sulphuretted hydrogen; and the filtrate evaporated in vacuo yields the hydrated acid in the form of a syrup, which does not crystallize and appears to be partially decomposed.

The syrupy acid when heated gives off pungent acid vapours, and afterwards phosphoric ether, recognizable by its odour. The decomposition terminates with a violent frothing of the whole mass, and phosphoric acid remains behind.

The *Biethylophosphates* have the composition: $MO,2C^4H^5O,PO^5$. They appear to be all soluble in water.

Baryta-salt. — Formed by saturating the aqueous acid with carbonate of baryta. — Dissolves readily in water and dilute alcohol, and may be obtained in needles and laminæ.

Lime-salt. Obtained by adding carbonate or hydrate of lime to phosphoric acid which has been left to deliquesce over alcohol or ether, or to the aqueous acid prepared by decomposing the lead-salt with sulphuretted hydrogen, — or by decomposing the lead-salt with an alcoholic solution of chloride of calcium.

Very soluble in water, less soluble in dilute alcohol, sparingly in absolute alcohol. Crystallizes on cooling from a warm, concentrated, aqueous solution, or from an aqueous solution gradually evaporated, — in silky groups of crystals like the lead-salt. From the solution in dilute alcohol it crystallizes in needles. When strongly heated, it does not give off water or fuse, but decomposes with evolution of phosphoric ether, turning slightly black at the same time.

			Vögeli.
CaO	28·0	16·39	16·23
PO^5	71·4	41·06	41·55
8 C	48·0	27·60	27·52
10 H	10·0	5·75	6·01
2 O	16·0	9·20	9·20
$CaO,2C^4H^5O,PO^5$	173·4	100·00	100·51

Magnesia-salt. — Formed by decomposing the lead-salt with sulphate of magnesia. Very soluble in water; crystallizes with difficulty.

Nickel-salt. — Obtained in a similar manner. Solidifies from a warm concentrated solution, in laminæ united in groups and containing water of crystallization. Very soluble.

Lead-salt. — The preparation of this salt has been already described. It dissolves readily in cold water, still more in warm water; readily also

in dilute alcohol, very slowly in cold absolute alcohol, very easily in warm alcohol of 40°. The aqueous solution slowly evaporated at a gentle heat yields the salt in beautiful needles, often of measurable size. From a warm concentrated solution it solidifies on cooling in groups resembling theïn; from a solution in warm absolute alcohol, it separates on cooling in crystalline masses having a silky lustre. Absolute alcohol affords the readiest method of purifying the salt, separating it at once from insoluble lead-salt and free acid, without the trouble of repeated crystallization. — The salt fuses at 180°, and solidifies again at 175° in a stellate crystalline mass, which redissolves almost completely in water. When heated above its melting point, it decomposes, giving off white vapours of phosphoric ether.

			Vögeli.
PbO	112·0	43·44	43·41
PO^5	71·4	27·77	27·53
8 C	48·0	18·66	18·36
10 H	10·0	3·90	3·98
2 O	16·0	6·23	6·72
$PbO,2C^4H^5O,PO^5$	257·4	100·00	100·00

Copper-salt. — Obtained by decomposing the lead-salt with sulphate of copper. Very soluble in water; could not be obtained in the crystalline state. (Vögeli.) ¶

Sulphide of Ethylene and Hydrogen? $C^4H^6S^4 = C^4H^4S^2,2HS$.

LÖWIG & WEIDMANN. *Pogg.* 49, 132; also *J. pr. Chem.* 19, 434.

A mixture of the alcoholic solution of sulphide of hydrogen and potassium and Dutch liquid set aside in a stoppered bottle, deposits a large quantity of chloride of potassium. The colourless liquid decanted therefrom yields an alcoholic solution of sulphide of ethylene and hydrogen, contaminated, however, with a small quantity of hydrosulphuric acid, which may be removed by means of acetate of lead:

$$C^4H^4Cl^2 + 2(KS,HS) = C^4H^6S^4 + 2KCl.$$

The liquid has an offensive odour, like that of hydrosulphuric acid. When diluted with water (whereupon it becomes turbid after a while) it forms a sulphur-yellow precipitate with lead salts (changing to white after a while), green with ferric salts, blue with cupric salts, white with corrosive sublimate, and yellow with nitrate of silver, terchloride of gold, and bichloride of platinum.

The lead-precipitate.			Löwig & Weidmann.
2 Pb	208	69·33	68·05
4 C	24	8·00	8·71
4 H	4	1·34	1·71
4 S	64	21·33	21·60
	300	100·00	100·07

Sulphite of Sulphethyl? or Hyposulphite of Ethylene?

$C^4H^5S^2O^2 = C^4H^5S,SO^2$? or $C^4H^4S^2O^2 = C^4H^4,S^2O^2$?

LÖWIG & WEIDMANN. *Pogg.* 49, 324.
H. KOPP. *Ann. Pharm.* 35, 343.

When dilute nitric acid is digested with excess of mercaptan, the mixture assumes a red colour, and after a while deposits an oil. The mixture is digested for some time with occasional addition of nitric acid, till the mercaptan is wholly or for the most part decomposed — but not too long, because in that case nothing but ethylosulphurous acid would be produced;—the hot liquid is then immediately diluted with a large quantity of water to prevent further decomposition; the oil separated from the watery liquid; kept for some time between 60° and 70° to volatilize the excess of mercaptan; then distilled with water, and dried by means of chloride of calcium. (Löwig & Weidmann). — The oil, together with the nitric acid liquid, must be thrown upon a wet filter which will not let the oil pass through; then well washed with water, and dried over chloride of calcium, which likewise removes the yellowish colour after acting for some time. (H. Kopp.)

Transparent and colourless oil, heavier than water (of sp. gr. 1·24, Kopp); boils between 130° and 140°, and may be distilled with water without alteration, but when distilled alone, appears to be partially decomposed. Has a very offensive and persistent smell, resembling that of onions. (Löwig & Weidmann.)

Calculation *a*.			Calculation *b*.			Löwig & Weidmann.	H. Kopp.
4 C	24	31·17	4 C	24	31·58	31·15	31·12
5 H	5	6·49	4 H	4	5·26	6·49	6·46
2 S	32	41·56	2 S	32	42·11	41·52	46·56
2 O	16	20·78	2 O	16	21·05	20·84	15·86
$C^4H^5S^2O^2$	77	100·00	$C^4H^4S^2O^2$	76	100·00	100·00	100·00

Löwig and Weidmann give the preference to calculation *a*; but the hydrogen comes too close to the quantity determined by analysis. The large quantity of sulphur found by Kopp (a sample which still retained a yellowish tint, yielded as much as 47·84 p. c.) renders the composition of this body still more doubtful.

The oil, when distilled alone, decomposes for the most part, leaving a porous, carbonaceous residue, and yielding a very pungent distillate, whose boiling point is about 55° but continually rises. Burns with a blue flame. Is blackened by warm oil of vitriol. (Kopp.) — When treated with nitric acid, it takes up 4 At. oxygen and is wholly converted in ethylosulphurous acid, $C^4H^5S^2O^6$ [$C^4H^6S^2O^6$]. — Digested with caustic potash, it is resolved into bisulphide of ethyl which separates, alcohol which may be distilled off, and bisulphethylosulphate of potash which, after the excess of potash has been removed by carbonic acid, and the solution evaporated to dryness over the water-bath, may be dissolved out by alcohol; $7C^4H^5S^2O^2 + 2HO = 2C^4H^6O^2 + 3C^4H^5S^2 + 2C^4H^5S^4O^6$. (Löwig & Weidmann.)

Sulphite of Ethyl. C^4H^5O,SO^2.

EBELMEN & BOUQUET (1845). *N. Ann. Chim. Phys.* 17, 66; also *J. pr. Chem.* 38, 223; abstr. *Compt. rend.* 20, 1592; 22, 370.

Sulphurous ether, Vinic or Ethylic Sulphite; schwefligsaurer Aether, schwefligsaures Aethyloxyd, Schwefligvinester, Sulfite d'oxyde d'Ethyle.

Absolute alcohol is added to chloride of sulphur as long as hydrochloric acid is evolved and sulphur precipitated—an action which is attended with great evolution of heat—and the liquid distilled. At first alcohol passes over containing a considerable quantity of hydrochloric acid; the heat then increases, the sulphur melts together into a mass, the residual liquid becomes transparent and acquires a red colour, and between 150° and 170°, the sulphurous ether passes over, while a considerable quantity of sulphur remains behind. The distillate is then twice submitted to fractional distillation, till it exhibits a constant boiling-point of 160°.

Transparent and colourless liquid of sp. gr. 1·085 at 16°. Boils at 160°. Vapour-density 4·78. Has an ethereal odour something like that of peppermint; tastes cooling at first, then burning, and leaves a sulphureous after-taste.

			Ebelm. & B.		Vol.	Density.
4 C	24	34·78	34·46	C-vapour	4	1·6640
5 H	5	7·25	7·62	H-gas	5	0·3465
S	16	23·19	23·08	S-vapour	½	1·1093
3 O	24	34·78	34·84	O-gas	1½	1·6639
C^4H^5O,SO^2	69	100·00	100·00	Ether-vapour	1	4·7837

The vapour is therefore monatomic, like that of vinic ether.

The vapour does not take fire, unless it be previously heated; it then burns with a bluish flame and a strong odour of sulphurous acid.—When kept in imperfectly closed vessels, it is decomposed by the action of the moist air which enters, and evolves sulphurous acid. When precipitated from its alcoholic solution by water, it dissolves in an excess of the water, but very slowly and with evolution of sulphurous acid. The solution of sulphurous ether in alcoholic potash likewise emits a strong odour of sulphurous acid when diluted with water and mixed with hydrochloric acid.—Chlorine gas acts violently upon it, even in diffused daylight; but the aid of sunshine is required to complete the decomposition into hydrochloric acid gas, sesquichloride of carbon (C^4Cl^6), chlorosulphuric acid ($SClO^2$), and chloraldehyde ($C^4Cl^4O^2$).

$$2C^4H^5SO^2 + 22Cl = C^4Cl^6 + 2SClO^2 + C^4Cl^4O^2 + 10HCl.$$

Chlorine therefore acts on sulphurous ether in the same manner as it would on oxide of ethyl and sulphurous acid separately, a fact which seems to favour the idea that these two compounds actually pre-exist in the compound ether.—Sulphurous ether exposed to sunshine in bottles filled with chlorine forms broad laminæ of C^4Cl^6, which dissolve as the remaining liquid becomes heated, and separate out again as it cools.

When the action is over, there is found beneath the laminæ a transparent and colourless liquid, which fumes strongly in the air, has a suffocating acid odour, and consists of a mixture of $SClO^2$ and $C^4Cl^4O^2$, in which a certain quantity of C^4Cl^6 is dissolved. It begins to boil below 100°, first yielding a colourless fuming distillate and a sublimate of C^4Cl^6, then blackening, while the boiling point rises to 160°....170°, and yielding a coloured distillate. Dry air passed through the liquid takes up the vapour of the chlorosulphuric acid, so that, if subsequently passed through water, it gives up hydrochloric and sulphuric acid to that liquid. The acid liquid sinks in water, partially dissolving therein with great evolution of heat and formation of gas bubbles which are reabsorbed. The substance which dissolves is chlorosulphuric acid; the oil which remains undissolved in cold water is chloraldehyde mixed with C^4Cl^6; it disappears in hot water by conversion into chloracetic acid, the compound C^4Cl^6 separating out. The acid liquid immersed in dry ammoniacal gas changes to a solid mass, which partly dissolves in water in the form of sal-ammoniac, sulphate of ammonia, and sulphamide (II, 455). From an aqueous solution of ammonia, the acid liquid throws down C^4Cl^6 and chloracetamide ($C^4NH^2Cl^3O^2$) with a hissing noise.

Sulphurous ether mixes in all proportions with ether and alcohol. (Ebelmen & Bouquet; *comp.* Hare, *Phil. Mag. J.* 42, 471.)

Ethylosulphurous Acid. $C^4H^6S^2O^6 = C^4H^6O^2,2SO^2$.

Löwig & Weidmann. *Pogg.* 47, 153; 49, 329.
Hermann Kopp. *Ann. Pharm.* 35, 346.

Weinschweflige Säure, Sulfäthylschwefelsäure (Lowig & Weidmann). *Hyposulpethylic acid, Bisulphethylic acid.* (Muspratt), *Acide éthylique sulfuré* (Gerhardt). Discovered by Löwig & Weidmann in 1839.—Produced by the action of nitric acid in excess upon mercaptan. Also by the action of nitric acid on sulphocyanide and bisulphide of ethyl. (Muspratt.)

Preparation. b. From Mercaptan. A small quantity of mercaptan is added to moderately strong nitric acid, which, together with the mercaptan floating upon its surface, is slowly converted into a red liquid and then gives off nitrous fumes with great evolution of heat; small quantities of mercaptan are continually added as often as the action slackens, but the mercaptan must not be added in excess. The resulting liquid contains, besides ethylosulphurous acid, a quantity of sulphuric acid greater in proportion as the nitric acid is more concentrated; the greatest quantity of ethylosulphurous acid is therefore obtained with dilute nitric acid aided by heat.—The liquid is evaporated over the water-bath to a syrup to drive off the remaining nitric acid; the syrupy residue dissolved in water; the solution saturated with carbonate of baryta; filtered to separate the sulphate of baryta, and lastly evaporated and cooled, whereupon the ethylosulphite of baryta separates out in crystals. These crystals are dissolved in water; the baryta precipitated by a slight excess of sulphuric acid; the filtrate digested with carbonate of lead, till a portion of the lead is dissolved; the lead precipitated from the filtrate by sulphuretted hydrogen; the liquid again filtered; and the acid concentrated by evaporation. (Löwig & Weidmann.)

¶ 2. *From Sulphocyanide of Ethyl.* *a.* When sulphocyanide of ethyl is distilled with an equal weight of moderately strong nitric acid, a violent action takes place, nitrous acid, nitric oxide, and carbonic acid are evolved, and sulphuric acid is formed in greater quantity as the nitric acid is stronger. If the distillate be poured back again and the contents of the retort finally evaporated in the water-bath till the nitric acid is completely expelled, ethylosulphurous acid remains in the form of an oily liquid, resembling oil of vitriol and having an alliaceous odour. To purify this product, it is saturated with carbonate of baryta, the baryta-salt decomposed by sulphuric acid, the filtrate saturated with carbonate of lead, the liquid again filtered, and the lead precipitated by sulphuretted hydrogen; on evaporating the filtrate, the acid is obtained in the pure state. (Muspratt, *Chem. Soc. Qu. J.* 1. 47.) — *β.* The acid is also obtained by acting on sulphocyanide of ethyl with a mixture of chlorate of potash and hydrochloric acid:

$$\underbrace{C^4H^5,C^2NS^2}_{\text{Sulphocyanide of ethyl.}} + 3(KO,ClO^5) + 7HCl = \underbrace{C^4H^6O^2,2SO^2}_{\text{Ethylosulphurous acid.}} + 2CO^2 + NO^2 + 3KCl + 6HO + 7Cl.$$

A violent action takes place, sometimes sufficient to inflame the volatile products. On evaporating to dryness over a water-bath, treating the residue with absolute alcohol to remove chloride of potassium and any sulphate of potash that may have been formed, and evaporating the filtered alcoholic solution, an oily acid is left whose baryta-salt was found by Muspratt to agree in composition with that of ethylosulphurous acid. (*Chem. Soc. Qu. J.* 1, 50.) — 3. *From Bisulphide of Ethyl.* When equal parts of bisulphide of ethyl and moderately strong nitric acid are gently heated in a retort, a very violent action is produced; nitrogen, carbonic acid and nitrous acid are given off; sulphuric acid is formed, in quantity depending on the strength of the nitric acid used; and a liquid is obtained which, when evaporated over the water-bath, yields an oily acid, having an alliaceous odour, and identical with that which is obtained by the preceding method; it may be purified in a similar manner. (Muspratt, *Chem. Soc. Qu. J.* 1, 51; 3, 20.) — From his first experiments on the acid prepared in this manner, Muspratt concluded that it was a peculiar acid, which he called Bisulphethylic acid, containing 1 At. oxygen less than the acid obtained from sulphocyanide of ethyl; but subsequent researches convinced him of the identity of the two. (*Compare* VII, 298.) ¶

Properties. The acid is a heavy oil (of sp. gr. 1·30, according to Kopp), in which, especially in the cold, transparent and colourless crystals form after a while. It is inodorous, and tastes strongly acid, leaving a very unpleasant after-taste, which recalls the odour of phosphuretted hydrogen. (Löwig & Weidmann.) — ¶ According to Muspratt, the acid (obtained from bisulphide of ethyl), when left in a cold place over sulphuric acid in vacuo, yields colourless needles, extremely deliquescent and having a faint odour of garlic. Its taste is very disagreeable and acrid. ¶

			Kopp.
4 C	24	21·82	22·26
6 H	6	5·45	6·14
2 S	32	29·09	
6 O	48	43·64	
$C^4H^6O^2,2SO^2$	110	100·00	

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

			L. & W. at 120°.	Kopp. at 100°.
K[illegible]	[illegible]	[illegible]	31·31	31·25
[illegible]	[illegible]	[illegible]	15·54	16·24
[illegible]	[illegible]	[illegible]	4·01	4·[illegible]
[illegible]	[illegible]	[illegible]		
[illegible]	[illegible]	[illegible]		
C·H·K[illegible]	[illegible]	[illegible]		

Löwig & Weidmann found in the fused salt 33·42 per cent. of KO; 31·31 p. c. in the salt dried at 120°; and 30·41 p. c. in the crystallized

salt; and since the crystallized salt gives off 6·75 p. c. of water at 120°, and an additional quantity when fused, the crystallized salt is, according to them, KO,C^4H^5SO,SO^3; after drying at 120°, it contains 1 Aq. and in the crystallized state 2 Aq. It remains to be determined whether the loss of water at the melting-heat amounts to 1 At. and whether this water is not, even at that temperature, mixed with products of decomposition.

Ethylosulphite of Soda. — May be obtained by the same two processes. The crystals contain water, and cannot be melted without decomposition. They deliquesce slowly in the air, dissolve slowly in cold alcohol, and crystallize from the solution in hot alcohol. (Löwig & Weidmann.)

Dried at 100°.			Kopp.
NaO	31·2	23·60	23·16
4 C	24·0	18·15	17·60
5 H	5·0	3·78	3·91
2 S	32·0	24·21	26·61
5 O	40·0	30·26	28·72
$C^4H^5NaO^2,2SO^2$	132·2	100·00	100·00

Ethylosulphite of Baryta. — This salt with 1 At. water forms transparent, colourless, oblique rhombic tables, having the disagreeable taste of the acid. They give up their water, amounting to 5·19 per cent. (5·4 according to Kopp) below 100°; according to Muspratt, they give off 5·02 at 100°. The residue begins to blacken at a very strong heat, then gives off sulphureous, empyreumatic products, which have an offensive odour and burn with a violet flame, — and leaves a carbonaceous pyrophoric residue. After fusion with hydrate of potash, the salt gives off sulphurous acid, while sulphate of baryta remains undissolved. — The salt dissolves readily in water, and to a certain extent in hydrated alcohol, but not in absolute alcohol, which indeed, when added to the solution in hydrated alcohol, precipitates the salt after a while in white crystalline flocks. (Löwig & Weidmann.)

		Löw. & W. at 120°.			Muspratt. (*a*) at 100°.		(*b*) at 100°.
BaO	76·6	43·13	44·74	43·66	42·69	43·26	43·30
4 C	24·0	13·51	14·40	14·24	13·76	13·16	13·53
5 H	5·0	2·82	3·09	3·12	3·21	3·05	3·00
2 S	32·0	18·02	19·51	19·19	17·99	17·56	17·75
5 O	40·0	22·52	18·26	19·79	22·35	22·97	22·42
$C^4H^5BaO^2,2SO^2$	177·6	100·00	100·00	100·00	100·00	100·00	100·00

The two analyses by Muspratt, marked (*a*), were made with a salt of the acid prepared from sulphocyanide of ethyl; (*b*) from the bisulphide.

Ethylosulphite of Lime. — The aqueous acid saturated with carbonate of lime yields on cooling, transparent and colourless crystals, which resemble those of the baryta-salt, but dissolve readily, not only in water but likewise in alcohol, (Löwig & Weidmann.)

Dried at 100°.			Kopp.
CaO	28	21·71	22·65
4 C	24	18·60	17·94
5 H	5	3·87	4·08
2 S	32	24·81	24·22
5 O	40	31·01	31·11
$C^4H^5CaO^2,2SO^2$	129	100·00	100·00

Ethylosulphite of Magnesia. — Crystallizes on cooling in prisms which give off their water of crystallization when heated and dissolve readily in water and alcohol. (Löwig & Weidmann.)

Ethylosulphite of Manganese. — The hot saturated solution of carbonate of manganese in the aqueous acid, yields the salt in colourless needles readily soluble in water and alcohol. (Löwig & Weidmann.)

Ethylosulphite of Zinc. — Obtained in a similar manner. Indistinct crystals united in dendritic masses; they effloresce in dry air, but absorb water in a moist atmosphere. The crystallized salt fuses when heated, and solidifies in a crystalline mass on cooling. At 120° it gives off 8·72 p. c. (2 At.), and in all 22·96 p. c. (5 At.) in all at 180° of water. But the salt dried at 180° still retains 3 At. water; for analysis shows it to contain only 24·85 p. c. ZnO; 15·48 C. and 5·08 H. — The salt dissolves readily in water and alcohol. (Löwig & Weidmann.)

Ethylosulphite of Lead. — The aqueous acid saturated at a boiling heat with carbonate of lead yields on cooling, laminæ and tables which gives off 2·2 p. c. ($\frac{1}{2}$ At.) water at 120°, (4 p. c. = 1 At. at 100°, according to Muspratt); fuse with intumescence at a stronger heat; and leave a considerable quantity of sulphite of lead in the residue. (Löwig & Weidmann.) — Soluble in alcohol both absolute and hydrated. (Muspratt.)

	Dried at 120°.		Löw. & W.	Kopp.	Muspratt.
PbO	112	52·58	51·45	52·55	52·76
4 C	24	11·27	11·98	11·22	
5 H	5	2·35	2·64	2·52	
2 S	32	15·02	15·83	15·69	
5 O	40	18·78	18·10	18·02	
$C^4H^5PbO^2,2SO^2$	213	100·00	100·00	100·00	

Ferrous Ethylosulphite. — Iron dissolves in the boiling concentrated acid, which then, on cooling, deposits colourless prisms readily soluble in water and alcohol. (Löwig & Weidmann.)

Ethylosulphite of Copper. — Obtained by saturating the aqueous acid with carbonate of copper. Light blue, transparent crystals, which have exactly the same form as the baryta-salt, give off 10·36 p. c. (2 At.) water at 120°, and dissolve readily in water and alcohol. (Löwig & Weidmann.) The crystals heated in a tube, intumesce, turn black and give off vapours having a very disagreeable odour. (Muspratt.)

	a. *Dried at* 120°.		L. & W.		b. *Crystallized.*		L. & W.
CuO	40	23·81	23·28				
4 C	24	14·29	15·00	a.	168	90·32	89·64
8 H	8	4·76	5·67	2 Aq.	18	9·68	10·36
2 S	32	19·05	19·82				
8 O	64	38·09	36·23				
$C^4H^5CuO^2,2SO^2+3Aq.$	168	100·00	100·00	$+2Aq.$	186	100·00	100·00

	Crystallized.		Muspratt. α.	Muspratt. β.
CuO	40	21·50	21·68	
4 C	24	12·90	13·11	14·48
10 H	10	5·37	4·84	5·10
2 S	32	17·20		
10 O	80	43·03		
$C^4H^5CuO^2,2SO^2+5Aq.$	186	100·00		

Muspratt's analysis *a* was made with a salt prepared from acid obtained from sulphocyanide of ethyl; *β*, from the bisulphide of ethyl. To the latter Muspratt originally assigned the formula $CuO,C^4H^5S^2O^4 + 4Aq.$, which requires 14·20 p. c. carbon and 5·33 H. (compare page 407).

Ethylosulphite of Silver. — The solution of carbonate of silver in the hot aqueous acid solidifies on cooling in a colourless mass consisting of crystalline laminæ. The crystals heated in a glass tube, fuse with evolution of [adhering?] water, and form a colourless liquid, which, at a higher temperature, decomposes and becomes coloured. They dissolve in water and alcohol. (Löwig & Weidmann.)

Crystallized.			L. & W.
AgO	116	53·46	51·51
4 C	24	11·06	11·32
5 H	5	2·30	2·71
2 S	32	14·75	
5 O	40	18·43	
$C^4H^5AgO^2,2SO^2$	217	100·00	

Ethylosulphurous acid mixes in all proportions with alcohol and ether. (Löwig & Weidmann.)

Bisulphethylosulphuric Acid.

Löwig & Weidmann (1840.) *Pogg.* 49, 326.

Scarcely known otherwise than in combination with potash.

Aqueous sulphite of sulphethyl (p. 404) is digested with potash-ley; the bisulphide of ethyl and alcohol formed at the same time are distilled off; the excess of potash in the residual liquid saturated with carbonic acid; the solution evaporated to dryness over the water-bath, and the potash-salt extracted therefrom by alcohol. On evaporating the alcohol over the water-bath, there remains a yellowish syrup with traces of crystals; and after stronger concentration, which is attended with escape of water, the liquid on cooling yields delicate laminæ and needles. The salt dried at 140° is white and becomes carbonized at a stronger heat, with evolution of stinking sulphuretted products. The salt deliquesces in the air.

The aqueous solution of the potash-salt forms a black precipitate with mercurous nitrate, and white with corrosive sublimate. On lead, copper and silver salts, it exerts no action.

Dried at 100°.			Löwig & W.
2 KO	94·4	38·63	38·48
4 C	24·0	9·82	10·82
6 H	6·0	2·45	2·53
4 S	64·0	26·19	25·12
7 O	56·0	22·91	23·05
	244·4	100·00	100·00

The improbability of the formula deduced from this analysis renders further investigation desirable.

Sulphate of Carbyl. $C^4H^4,4SO^3$.

REGNAULT. *Ann. Chim. Phys.* 65, 98; also *Ann. Pharm.* 25, 32; also *J. pr. Chem.* 12, 109.
MAGNUS. *Pogg.* 47, 509.

Carbylsulfat, Acide sulfacetylique. Discovered in 1837 by Regnault; more minutely examined by Magnus.

Formed, with strong evolution of heat, when anhydrous sulphuric acid is brought in contact with olefiant gas, ether, or absolute alcohol.

Preparation. 1. When olefiant gas, previously purified by passing through potash and oil of vitriol, is passed simultaneously with the vapour of anhydrous sulphuric acid into a U-tube, the resulting compound collects on the sides of the tube in radiated masses. To saturate the sulphuric acid as completely as possible, olefiant gas is finally passed alone through the tube, which, at the same time, is heated to 50° or 60°; but a portion of the acid always remains uncombined, and may be recognised by the fuming of the mass. No other products are formed, — no hydrate of sulphuric acid for instance. (Regnault.) The purification of the resulting compound on earthenware plates (vid. *Preparation* 2) is difficult, because the compound is in the form of a dense crystalline mass. (Magnus.)

2. Vapour of anhydrous sulphuric acid evolved from fuming oil of vitriol heated in a retort, is condensed in cooled bottles, into one of which is introduced a glass tube half an inch wide, almost as long as the bottle, closed at bottom, and filled with absolute alcohol, and the bottle is closed and set aside. After the vapour of the acid has been gradually taken up by the alcohol—an action which is attended with the formation of crystals in the tube—the tube is transferred into a second bottle containing sulphuric acid, thence into a third, &c., so that the alcohol may be completely saturated with the acid. — As alcohol evaporates at the same time from the tube, it likewise unites with the sulphuric acid in the bottle and forms crystals which may be used for the preparation of ethionic acid. — To purify the crystals deposited in the tube, the supernatant fuming oil of vitriol is poured off; the crystals, which fume, in consequence of sulphuric acid adhering to them, are placed on a warm plate of baked clay, and introduced into a vacuum over common oil of vitriol, which absorbs the vapour of the anhydrous sulphuric acid, whilst oil of vitriol, sulphovinic acid, ethionic and isethionic acids sink into the plate; hence the plate must be renewed every day till the crystals no longer fume. They must then be sealed up in a glass tube. (Magnus.)

Properties. Colourless radiating crystals which melt at about 80°, and solidify again in the crystalline form on cooling. (Regnault.)

			Magnus. (1)	Magnus. (2)
4 C	24	12·77	12·23	12·88
4 H	4	2·12	2·75	2·69
4 SO^3	160	85·11		85·90
$C^4H^4,4SO^3$	188	100·00		101·47

The crystals deliquesce in the air and dissolve in water (also in alcohol) with evolution of heat, and form a solution of ethionic acid, $C^4H^6O^2,4SO^3$. In this action, 2 At. HO combine with the sulphate of carbyl; consequently it cannot be recovered by evaporating the solution. Small quantities of sulphuric and isethionic acid are also produced together with the ethionic acid, when the compound is dissolved in water. The sulphuric acid is precipitated on saturating the solution with baryta; it likewise shows itself when the sulphate of carbyl is left to deliquesce in air saturated with moisture, so that all rise of temperature is avoided; but it varies in quantity between 13 and 22 per cent. The sulphuric and isethionic acids should perhaps be regarded only as secondary products, inasmuch as ethionic acid may be resolved into them. (Magnus.) — Regnault found that $\frac{1}{8}$ of the sulphuric acid contained in the aqueous solution of the compound existed therein in the free state, and was therefore precipitated by baryta-water. He attributes it to the impossibility of completely removing the anhydrous sulphuric acid which adheres to the crystals, — as shown by their fuming in the air; the remaining portion of the sulphate of carbyl is, according to Regnault, converted into isethionic acid. We must however suppose, with Magnus, that when the compound is dissolved in water, ethionic acid, $C^4H^6O^2,4SO^3$, is first produced, and is afterwards, especially when heated, resolved into 2 At. free sulphuric acid and isethionic acid, $C^4H^6O^2,2SO^3$.

¶ Sulphate of Ethyl. $C^4H^5SO^4=C^4H^5O,SO^3$.

WETHERILL. *Ann. Pharm.* 66, 117; abstr. *Pharm. Centr.* 1848, 922; *N. J. Pharm.* 14, 225; *Jahresber.* 1847—8, 692.

Vinic or Ethylic Sulphate, Sulphuric ether. Discovered by Wetherill in 1848.

Formation. By the action of anhydrous sulphuric acid on ether or absolute alcohol — Part of the sulphuric acid however abstracts from the ether the elements of water, so that, on the one hand, the preceding compound $C^4H^4,4SO^3$ is formed, and on the other, sulphovinic and ethionic acids:

$$[4(C^4H^5O,SO^3) + 10SO^3 = \underbrace{2(C^4H^4,4SO^3)}_{\text{Sulphate of carbyl.}} + \underbrace{C^4H^6O^2,2SO^3}_{\text{Sulphovinic acid.}} + \underbrace{C^4H^6O^2,4SO^3}_{\text{Ethionic acid.}}]$$

Again, when anhydrous sulphuric acid comes in contact with absolute alcohol, it abstracts from the alcohol the elements of water, and the ether thus produced unites with another portion of the anhydrous sulphuric acid, forming sulphate of ethyl, while sulphovinic acid is at the same time produced. (Wetherill.)

Preparation. Vapour of anhydrous sulphuric acid is passed into ether contained in a flask surrounded with a freezing mixture. For this purpose, it is not necessary that the tube which conveys the acid vapour should dip into the ether, inasmuch as the vapour, from its great density, is sure to sink to the bottom of the flask, if merely introduced at the top. The liquid after a while acquires a syrupy consistence, and must then be shaken up with an equal bulk of ether and four times its bulk of water.

It then separates into two layers, the upper of which, containing the ethylic sulphate, must be separated from the lower, which is strongly acid, and contains sulphuric, sulphurous, ethionic, and sulphovinic acids, mixed, if the temperature has not been kept low enough, with black carbonaceous particles, and also with isethionic and methionic acids, resulting from the decomposition of the ethionic acid. The ethereal liquid is then shaken up with milk of lime to remove the sulphurous acid—whereby part of the colouring matter is at the same time removed—then washed with water, filtered, and the ether distilled off. In the retort there remains an oily liquid, containing a trace of ether and having a slightly acid reaction, arising from the decomposition of part of the ethylic sulphate, which takes place when the liquid is heated, by the action of the water taken up by the ether. The oil is then transferred from the retort into a basin, and washed with a small quantity of water, the last portions of which are carefully removed by strips of bibulous paper, after which the liquid is dried in vacuo over sulphuric acid. (Wetherill.)

Properties. Oily liquid, colourless when pure, but generally exhibiting a yellow tint. Has a sharp taste, and smells like oil of peppermint. Sp. gr. 1·120. Makes greasy spots on paper, which however disappear after a while. (Wetherill.)

			Wetherill.
4 C	24	31·17	30·65
5 H	5	6·49	6·30
O	8	10·39	11·36
SO^3	40	51·95	51·69
$C^4H^5SO^4$	77	100·00	100·00

1. *Decompositions.* This compound is very easily decomposed when heated in contact with the air, so that it can only be distilled in an atmosphere of carbonic acid. At 100°, vapours begin to rise which condense in small oily drops; between 110° and 120°, the oil passes over unchanged; but between 130° and 140°, the liquid blackens, gives off sulphurous acid and alcohol, and at a higher temperature, the same products mixed with olefiant gas. — 2. Ethylic sulphate heated with *water*, forms, without separation of wine-oil, a very acid liquid, which gives off alcohol when boiled, and when treated with carbonate of baryta, yields three soluble baryta-salts, viz. methionate, sulphovinate and isethionate of baryta. The first of these salts is however so small in quantity, that it can only be regarded as a secondary product. The formation of the other products may be represented by the following equation:

$$3(C^4H^5O,SO^3) + 3HO = \underbrace{C^4H^5O^2,2SO^3}_{\text{Isethionic acid.}} + \underbrace{HO,C^4H^5O,SO^3}_{\text{Sulphovinic acid.}} + \underbrace{C^4H^6O^2}_{\text{Alcohol.}}.$$

3. *Sulphuretted hydrogen* does not act on ethylic sulphate at ordinary temperatures; but *Sulphide of hydrogen and potassium* decomposes it, forming mercaptan and sulphate of potash:

$$C^4H^5O,SO^3 + KS,HS = C^4H^5S,HS + KO,SO^3.$$

4. Chlorine does not decompose sulphuric ether at ordinary temperatures but is absorbed by it, forming a green liquid, which, on the addition

water, yields the compound in its original state. — 5. *Potassium* does not act on sulphuric ether at ordinary temperatures, but on the application of heat, decomposes it, with evolution of light and heat, forming mercaptan, together with other products. — 6. Sulphuric ether dissolves in fuming *Nitric acid*, and is precipitated from the solution by water. On adding caustic potash till the liquid is nearly neutral and applying heat, *nitrous ether*, C^4H^5O,NO^3, is evolved. (Wetherill.) ¶

Ethylosulphuric or Sulphovinic Acid.

$C^4H^6O^2,2SO^3 = HOSO^3 + C^4H^5O,SO^2$.

DABIT. *Ann. Chim.* 34, 300; also *Crell. Ann.* 1802, 1, 394. — *Ann. Chim.* 43, 101; also *A. Trs.* 11, 2, 157.
SERTÜRNER. *Gilb.* 60, 53; 64, 67. — *Kastn. Arch.* 7, 436.
A. VOGEL. *Gilb.* 63, 81.
GAY-LUSSAC. *Ann. Chim. Phys.* 13, 76; also *Gilb.* 70, 403.
WITTING. *Repert.* 9, 349. — *Mag. Pharm.* 3, 36; 6, 314.
DALK. *Berl. Jehrb.* 1820, 382.
HEEREN. *Pogg.* 7, 193.
HENNEL. *Phil. Trans.* 1826, 240; also *Ann. Phil.* 27, 291; also *Schw.* 49, 158; also *Pogg.* 9, 12. — *Phil. Trans.* 1828, 365; also *Pogg.* 14, 273; abstr. *Schw.* 35, 116.
DUMAS & BOULLAY. *Ann. Chim. Phys.* 36, 300; also *J. Pharm.* 14, 7; also *Pogg.* 15, 20.
SERULLAS. *Ann. Chim. Phys.* 39, 153; also *Schw.* 55, 147; also *Pogg.* 15, 20.
LIEBIG & WÖHLER. *Ann. Pharm.* 1, 37; also *Pogg.* 22, 486.
LIEBIG. *Ann. Pharm.* 13, 27.
MAGNUS. *Pogg.* 27, 367; also *Ann. Pharm.* 6, 152.
R. F. MARCHAND. *Pogg.* 28, 454; 32, 345; 41, 595.
BERZELIUS. *Pogg.* 44, 369.
MITSCHERLICH. *N. Ann. Chim. Phys.* 7, 8.

Aetherschwefelsäure, Weinschwefelsäure, Schwefelweinsäure, Oenothionsäure (Sertürner), *Althionsäure* (Magnus), *Acide sulfovinique, Sulfate acide d'hydrogène carboné* (Serullas), *Sulfate acide d'Ether* (Serullas), *Bisulfate d'Ether* (Serullas), *Sulfate acide d'Oxyde d'Ethyle.* — Dabit, in 1800, showed that the residue of the preparation of ether contains an acid which forms easily soluble salts with baryta and lime; this acid he regarded as intermediate in its degree of oxidation between sulphurous and sulphuric acid; the charring of these salts by heat, which he had previously noticed, he attributed to admixture of wine-oil. These statements were regarded as improbable, and passed into oblivion, till Sertürner, in 1819, gave out that he had discovered in this ether-residue three peculiar acids related to each other, and composed of alcohol and sulphuric acid, viz. the *first, second,* and *third Sulphovinic acids,* the existence of the first of which, viz. sulphovinic acid, has been corroborated by subsequent observation. Whether Sertürner's second sulphovinic acid is ethionic or althionic acid, and the third perhaps isethionic acid, is difficult to decide, on account of the looseness of the statements which he has made respecting these acids.

Formation. 1. From alcohol and oil of vitriol (pp. 222 – 225.) — 2. From ether and oil of vitriol (pp. 186, 187.) — 3. From olefiant gas and oil of

vitriol (p. 168); 1 vol. oil of vitriol absorbs in 18 days about 85 vols. olefiant gas, without formation of sulphurous or carbonic acid, but producing sulphovinic acid. (Faraday, *Phil. Trans.* 1825, 448; 1826, 140; Hennel, *Phil. Trans.* 1826, 240; also *Pogg.* 9, 21, 22.) According to Liebig, on the other hand (*Pogg.* 31, 328; further, *Ann. Pharm.* 14, 150) oil of vitriol takes from olefiant gas scarcely anything but the alcohol and ether vapour which may be mixed with it (which indeed may form sulphovinic acid); but when once these compounds have been removed by the oil of vitriol, a fresh quantity of the latter absorbs only 1·4 times its volume of the purified olefiant gas, the quantity thus absorbed not increasing even after several weeks' contact.

Preparation. I. By first forming a sulphovinate, and then separating the acid from it.

1. *Preparation of the Sulphovinate.* *a.* Oil of vitriol and absolute or very highly rectified alcohol are mixed in about equal portions; the mixture heated more or less, and then diluted with water; the sulphuric and sulphovinic acids saturated with baryta, lime or oxide of lead, or their carbonates; the solution of the sulphovinate filtered from the insoluble sulphate, and evaporated carefully to the crystallizing point. — Sertürner applies only a gentle heat to the mixture of equal parts of alcohol and oil of vitriol; A. Vogel heats it till ether begins to escape, because the quantity of sulphovinic acid is thereby increased. Marchand uses absolute alcohol, and allows the temperature to rise only to 60°–70°. — *b.* Ether-vapour is passed into oil of vitriol as long as it is absorbed, the liquid left to stand for some hours, then diluted with water, saturated with carbonate of baryta, &c. (Liebig.)

2. *Separation of the Acid from the Sulphovinate of Baryta, Lime, or Oxide of Lead.* — The aqueous solution of either of these salts is precipitated by an equivalent quantity of sulphuric acid (Sertürner), — or, better, the baryta-salt by sulphuric acid, the lime-salt by oxalic acid, and the lead-salt by sulphuretted hydrogen — and the filtrate evaporated in vacuo over oil of vitriol (A. Vogel), or chloride of calcium (Marchand).

II. One part of sulphovinate of wine-oil is gently heated with 4 pts. of water, and the aqueous solution of sulphovinic acid separated from the wine-oil thereby set free. (Serullas, Liebig.)

Properties. When sufficiently concentrated by evaporation, it forms a transparent, colourless, oily liquid of sp. gr. 1·319, and having a very sour taste (A. Vogel); of sp. gr. 1·315 to 1·317 at 16° (Marchand); 1·215. (Duflos, *Kastn. Arch.* 12, 176.)

			Marchand. of sp. gr. 1·317.
4 C	24	19·05	
6 H	6	4·76	
2 O	16	12·70	
2 S	32	25·40	62·19
6 O	48	38·09	
$C^4H^6O^2,2SO^3$	126	100·00	

According to this experiment of Marchand's, the acid may be almost wholly dehydrated in vacuo. — According to Serullas, Berzelius (*Pogg.* 44, 369), and Liebig, the acid dried *per se* is $HO,SO^3 + C^4H^5O,SO^3$, and the hypothetically anhydrous acid = $C^4H^5O,2SO^3$. — According to Williamson, Gerhardt, and Chancel, the acid dried *per se* =

$\left.\begin{matrix}C^4H^5\\H\end{matrix}\right\}2SO^4$ or $\left.\begin{matrix}C^4H^5\\H\end{matrix}\right\}SO^4$, according to the atomic weights adopted. — According to Marchand (*J. pr. Chem.* 15, 1), hypothetically anhydrous sulphovinic acid contains the elements of ether and sulphuric acid, fused, as it were, into a whole, but in such a manner that they may, under certain circumstances, again unite in the form of sulphuric acid and alcohol or ether. — Gay-Lussac, from the solubility of the sulphovinates, was led to suppose that the acid contains hyposulphuric acid in combination with a product of the decomposition of alcohol, 1 At. oxygen from 2 At. sulphuric acid having combined with 1 At. hydrogen from the alcohol to form water. But while hyposulphuric acid, both in the free state and in its salts, is in many reactions resolved into sulphurous and sulphuric acid, sulphovinic acid, under the same circumstances, yields 2 At. sulphuric acid to 1 At. alcohol. — Heeren supposed it to be a compound of alcohol with hyposulphuric acid = $C^4H^6O^2,S^2O^5$. — Dumas & Boullay regarded the hypothetically anhydrous acid as hyposulphate of wine-oil = C^4H^3,S^2O^5. But wine-oil is not C^4H^3; and hypothetically anhydrous sulphovinic acid must be supposed to contain 4C, 5H, 2S, and 7O; hence Dumas & Boullay's formula gives 2H and 2O too little. — Faraday regarded the hypothetically anhydrous acid as bisulphate of ethylene = $C^4H^4,2SO^3$; but this formula is deficient by 1H and 1O. — Laurent (*Ann. Chim. Phys.* 66, 209,) formerly regarded the acid as a compound of aldehyde with 2 At. sulphurous acid, = $C^4H^4O^2,2SO^2$, in which formula there is also a deficiency of 1H and 1O.

Decompositions 1. The concentrated acid is resolved by heat into ether and a residue of hydrated sulphuric acid (Sertürner, Hennel); when boiled down to dryness, it gives off sulphurous acid and olefiant gas, and leaves charcoal. (Serullas.) — If it be left for some time in vacuo over oil of vitriol, after being completely concentrated therein, it gives off sulphurous acid gas, while sulphuric acid remains behind mixed with oily drops. (A. Vogel.) According to Serullas, it does not give off sulphurous acid, but probably alcohol vapour, and leaves sulphuric acid without oily drops. — 2. The acid when kept for a long time in the dilute state, is partly converted into sulphuric acid. (A Vogel, Mitscherlich, *N. Ann. Chim. Phys.* 7, 8.) — When the dilute acid is boiled, this decomposition into alcohol which goes off into vapour, and sulphuric acid which remains behind, takes place quickly. (Hennel, Serullas, H. Rose, *Pogg.* 48, 463.) — 3. Cold nitric acid does not decompose sulphovinic acid immediately; but hot nitric acid eliminates nitrous gas and leaves sulphuric acid. (A. Vogel.) — 4. When sulphovinic acid of sp. gr. 1·215 is dropped into oil of vitriol heated to 150°, the latter turns brown and gives off sulphurous acid gas, while drops of wine-oil separate out. (Duflos.) — 5. Chromic acid, manganate of baryta, and peroxide of lead decompose the dilute acid, with separation of drops of wine-oil, which float on the surface, and formation of sulphuric acid. (Duflos, *Kastn. Arch.* 12, 177.) — 6. When the concentrated acid is heated with glacial acetic acid, acetic ether distils over, while sulphuric acid remains behind. (Mitscherlich, *N. Ann. Chim. Phys.* 7, 10):

$$C^4H^6O^2,2SO^3 + C^4H^4O^4 = C^8H^8O^4 + 2(HO,SO^3).$$

Combinations. Sulphovinic acid mixes in all proportions with *Water.*

Sulphovinates or *Ethylosulphates.* — Sulphovinic acid has considerable

effloresces strongly during evaporation. The salt dissolves with tolerable facility in alcohol and ether. (Marchand.)

Crystallized.			Marchand.	Or:			Regn.
NH^3	17	11·89	11·69	4 C	24	16·78	16·32
HO	9	6·30		9 H	9	6·30	6·41
C^4H^5O	37	25·87		O^2,N	30	20 98	
2 SO^3	80	55·94	55·99	2 SO^3	80	55·94	
$C^4H^5(NH^4)O^2,2SO^3$	143	100·00			143	100·00	

Sulphovinate of Potash. — Obtained by precipitating the baryta or lime-salt with carbonate of potash, evaporating the filtrate to the crystallizing point, and purifying the crystals by recrystallization from water. — Shining, unctuous scales, like those of crystallized boracic acid, and having a sweetish taste. (A. Vogel.) When the aqueous solution is left to evaporate spontaneously, during which a considerable portion of the salt effloresces out, large, transparent, colourless tables are obtained, belonging to the oblique prismatic system, and having a sweetish, saline, cooling taste; they do not contain water of crystallization, and do not diminish in weight when left in vacuo over oil of vitriol. (Marchand.) According to Liebig also, the salt, when placed in vacuo, remains transparent and does not diminish in weight.

Crystallized.			Hennel.	Or:			Marchand.
KO	47·2	28·74	28·80	KO,SO^3	87·2	53·11	52·62
2 SO^3	80·0	48·72	48·00	SO^3	40·0	24·36	24·59
4 C	24·0	14·62	13·98	4 C	24·0	14·62	14·43
4 H	4·0	2·44	2·34	5 H	5·0	3·04	3·11
HO	9·0	5·48	7·00	O	8·0	4·87	5·25
$C^4H^5KO,2SO^3$	164·2	100·00	100·12		164·2	100·00	100·00

The salt, when subjected to dry distillation, does not give off water, but melts and froths up, emitting white fumes which condense to sulphovinate of wine-oil having a strong odour of sulphurous acid, while acid sulphate of potash remains behind. (Hennel, Serullas.) The salt begins to decompose at 100°, and without fusing, yields sulphovinate of wine-oil mixed with sulphurous acid, olefiant gas and other combustible gases, together with sulphuric acid, while sulphate of potash mixed with charcoal remains behind. (Marchand.) — The salt fuses in the air at a gentle heat, burns with flame in a red-hot crucible, and leaves a mixture of charcoal and sulphate of potash. (A. Vogel.) — Mixed with hydrate of potash and subjected to dry distillation, it yields a large quantity of alcohol, to the formation of which the water of the hydrate contributes, and yields a residue containing nothing but sulphate of potash, and no sulphite. The salt, when heated with dry alkalis, also yields alcohol, but mixed with wine-oil and olefiant gas. (Marchand.) The aqueous solution of the salt is not decomposed by boiling with excess of potash. (Mitscherlich.) Respecting the distillation of the potash-salt with ferrocyanide and sulphocyanide of potassium, *vid.* Gregory, (*Ann. Pharm.* 27, 272.)

1 pt. of the salt dissolves in 0·8 pt. water at 17°. The salt deliquesces in moist air, dissolves in aqueous ammonia, producing great cold, and separates out again in the pure state when the solution is left to spontaneous evaporation. (Marchand.) It dissolves readily in aqueous alcohol (Hennel), but not in absolute alcohol or in ether. (Marchand.)

Sulphate of Potash and Ammonia? — The aqueous solution of 6 pts. ammoniacal salt and 7 pts. potash-salt yields by spontaneous evaporation

	Crystallized.			Marchand.
$C^4H^5LO^2,2SO^3$	131·4	87·95		88
2 Aq.	18·0	12·05		12
$C^4H^5LO^2,2SO^3+2Aq.$	149·4	100·00		100

Sulphovinate of Baryta. — Preparation (p. 416). — Transparent, colourless, shining, elongated tables (A. Vogel); rhombic prisms acuminated with four faces resting on the lateral edges (Gay-Lussac); square tables (Liebig & Wöhler); tables belonging to the right prismatic system (Marchand.) They are permanent in the air, and have a burning taste. (Dalk.) — The crystals contain 8·21 p. c. (2 At.) water, which they give off completely and without further decomposition, in vacuo over oil of vitriol, also between 50° and 55° in a current of dry air; but boiling alcohol abstracts only 1 At. of the water. (Marchand.) If an attempt be made to dry the crystals in the air, only a little above 20°, they turn white and no longer dissolve completely in water; if dried between 25° and 30° and triturated, they yield a powder which is permanent in the air; but when dried between 40° and 45°, they can no longer be rubbed to powder, but quickly deliquesce in the air, and form an acid liquid which deposits a large quantity of sulphate of baryta. (Liebig & Wöhler.) — The crystals cannot be deprived of more than 1 At. water, without decomposition; when heated to 50° in a current of air, till the evolved vapour begins to taste of alcohol, they give off 3·68 p. c., and the residue, when dissolved in water, leaves but a small quantity of sulphate of baryta; if only 3 per cent. of water has been thus driven out, the residue dissolves completely in water. (Magnus.) — Duflos estimates the loss of the crystals in vacuo over oil of vitriol at 13·1 per cent.

	Dehydrated.		Marchand.
BaO,SO^3	116·6	60·23	59·95
SO^3	40·0	20·66	
4 C	24·0	12·40	
5 H	5·0	2·58	
O	8·0	4·13	
$C^4H^5BaO^2,2SO^3$	193·6	100·00	

			Gay-Lussac.	Dumas & Boullay.	Liebig & Wöhler.	Liebig.	March.
BaO,SO^3	116·6	55·11	54·93	53·65	54·99		55·10
SO^3	40·0	18·90		18·44	19·72		
4 C	24·0	11·34		10·83	12·37	11·51	
7 H	7·0	3·31		3·60	3·06	3·17	
3 O	24·0	11·34			9·86		
+2Aq.	211·6	100·00			100·00		

100 pts. of the crystallized salt mixed and detonated with carbonate and chlorate of potash, then suspended in water, supersaturated with hydrochloric acid, and mixed with chloride of barium, yield 111·47 pts. (112·32, according to Liebig & Wöhler) of sulphate of baryta, consequently nearly double of that which remains when the salt is ignited alone. (Gay-Lussac.)

The crystals, when kept in a dry stoppered bottle for a year, become greyish and pasty, acquire the power of reddening litmus, and evolve an odour of ether. (Serullas, *J. chim. méd.* 6, 684.) In vacuo at 160°, the crystals suffer a loss of 19·31 to 20·00 per cent. but become pasty at the

same time, from formation of wine-oil. (Dumas & Boullay.) — Even between 100° and 110° they yield alcohol, wine-oil, combustible gases, &c. (Marchand.) The salt, when subjected to dry distillation, yields an empyreumatic ethereal liquid, a heavy oil, and a carbonaceous residue. (Vogel); water, a gas which burns like olefiant gas, an oil which smells like acetic ether, together with sulphurous acid, and a very small quantity of carbonate and sulphate of baryta. (Gay-Lussac.) — The crystals, after being triturated with ignited carbonate of potash, do not blacken when heated, but yield alcohol having a faint odour of ether. (Liebig & Wöhler.) In an open red-hot crucible, the salt blackens, burns with a bright blue flame, and leaves sulphate of baryta. (Gay-Lussac.) — The aqueous solution is decomposed by heat. (Gay-Lussac.) — When chlorine gas is passed through the solution, it remains clear, but deposits crystalline grains of sulphate of baryta when evaporated. When chlorine gas is passed over the heated crystals, a large quantity of a chloride of carbon is formed at the same time, which separates in oily drops, having a pungent odour and attacking the eyes strongly. (Liebig & Wöhler.)

The crystallized salt dissolves in 0·92 pt. water at 17°; it dissolves in [hydrated ?] alcohol (Magnus), but not in cold absolute alcohol; boiling absolute alcohol abstracts 1 At. water of crystallization from a portion of the salt, and dissolves another small portion, which separates out again in the form of an alcoholate as the liquid cools. (Marchand.)

Sulphovinate of Strontia. — Separates in large anhydrous crystals when the aqueous solution is left to evaporate spontaneously. The aqueous solution, even when largely diluted, is resolved by boiling into alcohol which evaporates, and sulphate of strontia which is precipitated. The crystals dissolve very readily in alcohol, but are insoluble in ether.

Crystallized.			Marchand.
SrO,SO^3	92	54·44	54·1
SO^3	40	23·66	
C^4H^5O	37	21·90	
$C^4H^5SrO^2,2SO^3$	169	100·00	

Sulphovinate of Lime. — (For the preparation see page 416). The solution, after a piece of chalk has been put into it to keep it neutral, must be evaporated at a gentle heat to a syrupy consistence, then filtered again from the sulphate of lime which has been formed, and left in a cold place. (Sertürner, Vogel, Heeren.) — Elongated, four-sided tables with bevelled corners (Vogel); thin rectangular tables (Heeren); thin transparent, colourless, nacreous, four and eight-sided tables, with cleavage parallel to the tabular face. (Marchand.) Of sweetish taste; permanent in the air when in regular crystals, but less perfect crystals become moist by exposure to the air (Vogel); very permanent. (Marchand.) — The crystals, when placed in vacuo over oil of vitriol, become opaque from loss of water (A. Vogel); they then give off 11·0 p. c. (2 At.) water (Marchand); 11·2 p. c. (Liebig); also at 80° in the air, without fusing. (Marchand.)

Dried in vacuo with oil of vitriol.			Heeren.	Serullas.	Liebig.
CaO,SO^3	68	46·89	47·24	45·05	47·32
SO^3	40	27·59	27·63	28·40	
4 C	24	16·55	14·59	15·21	
5 H	5	3·45	3·58	3·49	
O	8	5·52	6·96		
$C^4H^5CaO,2SO^3$	145	100·00	100·00		

	Crystallized.		Liebig.	Marchand.
CaO,SO^3	68	41·72	42·18	41·98
SO^3	40	24·54	24·61	
4 C	24	14·72	14·71	
7 H	7	4·30	4·28	
3 O	24	14·72	14·22	
$C^4H^5CaO^2,2SO^3+2Aq$	163	100·00	100·00	

100 pts of the salt dried in vacuo, and repeatedly distilled with water, yield a distillate containing 28·33 pts. of absolute alcohol, (Serullas.) According to calculation (145 : 46 = 100 : x), the quantity of absolute alcohol obtained should be 31·72 pts.

The crystals, when slowly heated in a retort, swell up, blacken, and yield an empyreumatic ether, a colourless oil which sinks in water and smells like oil of wine, lastly sulphurous acid, and leave a mixture of sulphate of lime and charcoal. (A. Vogel.) The dry salt sustains a temperature of 100° without decomposition, and at 110° yields pure ether, which however at a later stage of the process, becomes mixed with oil of wine and other products; if the heat be carefully raised, a carbonaceous residue remains; if it be suddenly raised, a very large quantity of wine-oil is obtained. (Marchand.) Sertürner states that he has obtained by dry distillation, a gas having an agreeable odour of ether, together with sulphurous acid, oil of vitriol, and three very volatile acids resembling succinic acid. — In an open crucible, the salt burns with a bright blue flame, and leaves sulphate of lime. (Vogel.) The aqueous solution turns sour when heated. (Sertürner.) — 1 pt. of the salt dissolves in 1 pt. of water at 8°, in 0·8 pts. at 17°, in 0·63 pt. at 30°, and in any quantity of boiling water. Alcohol first abstracts water from the crystals, and then dissolves the salt, though not so quickly as water; ether does not dissolve it, but throws it down from its alcoholic solution. (Marchand.)

Sulphovinate of Lime and Soda? — The aqueous solution of the two salts in about equal parts, yields needles having a silky lustre. (Marchand.)

Sulphovinate of Magnesia. — Formed by precipitating the baryta-salt with sulphate of magnesia. Square tables and prisms containing 4 At. water, none of which goes off in the air at 60° or 70°, but half at 80°; in vacuo over oil of vitriol also, 9·98 p. c. (2 At.) go off in two days, the other half escaping completely without further decomposition at 90° in the air, or in the course of 6 or 8 weeks in vacuo. — The salt dissolves very readily in water, but not in alcohol or ether; the aqueous solution is more inclined to decomposition than that of other sulphovinates. (Marchand.)

	Dehydrated.					
MgO,SO^3	60	43·80	44·11	MgO,SO^3	60	34·68	35·05
SO^3	40	29·20		C^4H^5O,SO^3	77	44·51	
C^4H^5O	37	27·00		4 Aq.	36	20·81	
$C^4H^5MgO,2SO^3$	137	100·00		$+4Aq$	173	100·00	

Sulphovinate of Alumina. — The aqueous solution decompose to a certain extent by evaporation at a gentle heat, and even by evaporation in vacuo at ordinary temperatures; in the latter case, it yields a gummy residue which deliquesces in the air and dissolves in alcohol. (Marchand.)

Uranous Sulphovinate. — Formed by precipitating the baryta-salt with uranous sulphate; the filtrate, when evaporated, effloresces for the most part in the form of a cauliflowerlike mass, and slowly yields crystals containing water. The salt is easily decomposed by boiling its aqueous solution; it deliquesces in the air, and dissolves in alcohol but not in ether. (Marchand.)

Uranic Sulphovinate. — The solution of hydrated uranic oxide in the aqueous acid dries up to a yellow saline crust on evaporation. This crust decomposes between 60° and 70°, after giving off water; towards water, alcohol, and ether, it behaves like the uranous salt. (Marchand.)

Manganous Sulphovinate. — Very stable, aurora-red tables containing 19·6 p. c. (4 At.) water, the whole of which is given off in 10 weeks when the crystals are left in vacuo over oil of vitriol at a temperature of 20° — 22°. — The salt dissolves readily in water and alcohol, but is insoluble in ether, which in fact precipitates the alcoholic solution. (Marchand.)

Dehydrated.							Marchand.
MnO	36	23·53	MnO	36	19·05		19·00
2 SO^3	80	52·29	$C^4H^5O,2SO^3$	117	61·90		
C^4H^5O	37	24·18	4 Aq	36	19·05		19·60
$C^4H^5MnO^2,2SO^3$	153	100·00	+4Aq.	189	100·00		

Sulphovinate of Zinc. — May be obtained by dissolving zinc in the aqueous acid, the solution being attended with evolution of hydrogen. — Large transparent and colourless tables, belonging to the oblique prismatic system, which give off all their water, amounting to 11·03 p. c. (2 At.), in vacuo over oil of vitriol, and likewise in the air between 50° and 60°. — The salt, when kept for some time in vacuo between 15° and 20°, gives off ether, and is converted into a moist mixture of sulphate of zinc and sulphuric acid. — The salt dissolves readily in water and alcohol, but not in ether, which indeed precipitates it from its alcoholic solution. (Marchand.)

Dehydrated.			*Crystallized.*			Marchand.
ZnO	40	25·48	ZnO	40	22·86	22·48
2 SO^3	80	50·95	C^4H^5O	117	66·86	
C^4H^5O	37	23·57	2 Aq.	18	10·28	11·03
$C^4H^5ZnO^2,2SO^3$	157	100·00	+2Aq.	175	100·00	

Sulphovinate of Zinc and Ammonium. — Formed by precipitating the dilute zinc-salt with ammonia, boiling till the excess of ammonia is expelled, and filtering. (Marchand.)

Sulphovinate of Cadmium. — Long, transparent, and colourless prisms, which give off 2 At. water in vacuo over oil of vitriol, and do not suffer much decomposition when kept in the vacuum for a longer time. Readily soluble in water and alcohol, but insoluble in ether. (Marchand.)

Sulphovinate of Lead. — *a. Bibasic.* — 1. Obtained by completely saturating with lead-oxide, a mixture of alcohol and oil of vitriol previously diluted with water. (A. Vogel.) — 2. By digesting aqueous sulphovinic acid or monobasic sulphovinate of lead with hydrated lead-oxide, till it is

saturated. (Marchand.) — By continued digestion with an excess of the hydrate, the liquid may even be rendered alkaline. (Dumas & Boullay.) The neutral filtrate, when evaporated at a gentle heat, yields a white mass. (Vogel.) In vacuo it dries up to a solid amorphous mass; when evaporated by heat, it is apt to turn brown, but may be decolorized again by boiling with animal charcoal. By dry distillation, the mass yields a colourless oil which sinks in water, a combustible liquid which smells like ether, also sulphurous acid, and finally sulphuric acid, leaving a residue of sulphate of lead mixed with charcoal. (Vogel.) When carefully heated, it yields nothing but alcohol and sulphovinate of wine-oil, for the preparation of which it may be used. (Marchand.) The aqueous solution is decomposed by rapid boiling, whereby sulphate of lead is precipitated; carbonic acid gas passed through it throws down carbonate of lead. (Vogel.) In close vessels, the solution remains unaltered for a long time; but when exposed to the air, it becomes covered with a crust of carbonate of lead, the formation of which goes on till the salt is converted into the monobasic salt. (Marchand.) — The dry salt becomes moist in the air, and dissolves in 0·5 pt. water (Vogel); in 0·54 water at 17°. (Marchand.) It dissolves in alcohol (Vogel) but not in ether. (Marchand.)

			Marchand.
2 PbO	224	65·69	64·67
2 SO^3	80	23·46	
C^4H^5O	37	10·85	
$PbO + C^4H^5PbO^2,2SO^3$	341	100·00	

b. Monobasic. — Formed by saturating pure sulphovinic acid, or the mixture of alcohol and oil of vitriol diluted with water, with carbonate of lead, and leaving the acid filtrate to evaporate spontaneously. Large transparent and colourless prisms, belonging to the right prismatic system. In vacuo over oil of vitriol, they give off 7·95 per cent. (2 At.) of water; also when heated in the air, whereby however a further decomposition is produced. As the heat increases, the crystals give off water at 80°, then ether, a large quantity of sulphovinate of wine-oil, a large quantity of sulphurous acid, and lastly also a certain quantity of sulphuric acid. Even at ordinary temperatures and in well closed vessels, they decompose by long keeping, so that in the course of half a year, they resolve themselves into ether, which may be recognized by its odour, and a small quantity of wine-oil, together with sulphate of lead and sulphuric acid; hence the crystals have a persistently pleasant odour. When the salt comes in contact with recently precipitated sulphide of lead, a compound resembling mercaptan is produced. — The salt dissolves readily in water and alcohol, but not in ether, which indeed precipitates it from its alcoholic solution. (Marchand.)

Dried in vacuo.			Marchand.	*Crystallized.*			
PbO	112	48·91	48·34	PbO	112	45·34	45·13
2 SO^3	80	34·93		$C^4H^5O,2SO^3$	117	47·37	
C^4H^5O	37	16·16		2 Aq.	18	7·29	7·95
$C^4H^5PbO^2,2SO^3$	229	100·00		+2Aq	247	100·00	

c. Bi-acid? — If the residue left in the preparation of ether be diluted with water and then treated with excess of carbonate of lead, the resulting liquid remains acid even on boiling, and after filtration,

evaporation and cooling, yields white, silky, transparent needles which redden litmus. (Dumas & Boullay.) — [Since Marchand adopted exactly the same process in preparing the normal salt (*b*), excepting that he did not make use of the ether-residue, it becomes a question whether the salt obtained by Dumas & Boullay was not derived from some acid different from sulphovinic acid, contained in the ether-residue.]

	Crystallized.		Dumas & Boullay.
PbO	112	31·55	31·49
4 SO^3	160	45·07	45·71
8 C	48	13·52	13·80
11 H	11	3·10	3·04
3 O	24	6·76	5·96
$C^4H^5PbO^2,2SO^3 + C^4H^6O^2,2SO^3$?	555	100·00	100·00

According to Dumas & Boullay, the formula of the salt is $PbO,2C^4H^3,2S^2O^5 + 5Aq$.

Sulphovinate of Lead and Ammonium. — Prepared by supersaturating the aqueous solution of monobasic sulphovinate of lead with ammonia; carefully evaporating the filtrate, whereupon ammonia evaporates and oxide of lead is precipitated; exhausting the residue with water; and evaporating the filtrate. This filtrate yields scales which resemble those of bimargarate of potash, and contain ammonia and oxide of lead. (Marchand.)

Ferrous Sulphovinate. — The aqueous acid dissolves iron, with evolution of hydrogen, and forms a colourless, sweetish liquid, which, when evaporated, yields yellow four-sided prisms, efflorescent in the air and easily soluble in water and alcohol. (A. Vogel.) According to Marchand, the prisms are greenish, contain water, decompose readily in the air, and are insoluble in ether.

Ferric Sulphovinate. — Obtained by dissolving the hydrated oxide in the aqueous acid, or by precipitating the baryta-salt with ferric sulphate. From the resulting solution, the salt crystallizes with difficulty in yellow tables which contain water of crystallization, deliquesce and decompose when exposed to the air, and dissolve readily in water and alcohol, but not in ether, which precipitates the salt from its alcoholic solution. (Marchand.)

Sulphovinate of Cobalt. — Large, dark red crystals, permanent in the air. They give off part of their water of crystallization in vacuo over oil of vitriol, and the whole, amounting to 9·5 per cent. (2At.), at 94° in the air. They contain 20 per cent. of oxide of cobalt. They dissolve readily in water and alcohol, but not in ether, which precipitates the alcoholic solution. (Marchand.)

Sulphovinate of Nickel. — Green granular crystals, containing 2 At. water of crystallization; they comport themselves like the cobalt-salt in vacuo, under the influence of heat, and also towards water, alcohol and ether. (Marchand.)

Sulphovinate of Copper. — Prepared by dissolving carbonate of copper in the aqueous acid (Vogel); or by precipitating the baryta-salt with sulphate of copper. (Dumas & Boullay; Marchand.) — Blue, four-sided prisms with bevelled summits (Vogel); blue eight-sided prisms, belonging to the right prismatic system. (Marchand.) Right rectangular prisms. (Regnault.) Dumas & Boullay, by evaporating the solution to a syrup,

and pressing the solidified granular mass into which the residue was converted on cooling, obtained the salt in greenish crystalline granules. Although the crystals contain 4 At. water, they nevertheless, when left in vacuo over oil of vitriol, even for 6 or 8 weeks, exhibit but a slight loss of weight, which is also accompanied by the formation of wine-oil and sulphuric acid. They likewise suffer no loss of weight when heated to 100° in the air, but at a somewhat higher temperature, they suddenly undergo complete decomposition. (Marchand.) In an open red-hot crucible, they burn with flame and leave sulphate of copper. (Vogel.) They dissolve very readily in water and alcohol (Vogel, Marchand), but not in ether, which precipitates the alcoholic solution. (Marchand.)

Crystallized.			Dum. & Boull.	March.	Magnus.
CuO	40	20·73	21·40	19·88	20·65
$2\,SO^3$	80	41·45	43·22		
4 C	24	12·43	12·42	12·78	
9 H	9	4·66	4·45	4·70	
5 O	40	20·73			
$C^4H^5CuO^2,2SO^3 + Aq.$	193	100·00			

According to Dumas & Boullay, who appeared to have examined a salt which had been altered in composition by evaporation at too high a temperature, the formula is: $CuO,C^4H^3,S^2O^5 + 5Aq$.

Mercuric Sulphovinate. — The solution of mercuric oxide in the aqueous acid, yields, when evaporated over oil of vitriol under a bell-jar not exhausted of air, a yellowish crystalline mass, which decomposes very readily, even at ordinary temperatures, deliquesces rapidly on exposure to the air, and is soluble in alcohol. (Marchand.)

Sulphovinate of Silver. — Prepared by digesting the aqueous acid with oxide or carbonate of silver till it is saturated, and evaporating. Small shining crystalline scales, containing 45·42 per cent. of oxide of silver, and therefore 2 per cent. water of crystallization, which they do not give off in vacuo, even in two days, but only at a heat at which further decomposition takes place. Soluble in water and alcohol. (Marchand.)

Isethionic Acid. $C^4H^6O^2,2SO^3$.

MAGNUS. *Pogg.* 27, 378; also *Ann. Pharm.* 6, 162.
LIEBIG. *Ann. Pharm.* 13, 32; 25, 39.
REGNAULT. *Ann. Chim. Phys.* 65, 98; also *Ann. Pharm.* 25, 32.
WOSKRESENSKY. *Ann. Pharm.* 25, 113.
BERZELIUS. *Pogg.* 44, 372; also *Ann. Pharm.* 28, 5.

Isäthionsäure, Acide isĕthionique. — Discovered by Magnus in 1833.

Formation. When anhydrous sulphuric acid is brought in contact with olefiant gas, ether, or alcohol, sulphate of carbyl (p. 413) is produced; this body, when dissolved in water, forms ethionic acid; and this acid is resolved by heat, whether produced by the sudden mixing with water or applied from without, into sulphuric and isethionic acid. (Magnus.) Oil of vitriol strongly heated with alcohol, likewise forms

isethionic acid, which therefore occurs in the residue of the ether-preparation. Oil of vitriol heated with ether, forms isethionic as well as sulphovinic acid. (Hennel.)

Preparation. Aqueous ethionate of baryta is decomposed by sulphuric acid, the liquid filtered from sulphate of baryta, boiled, saturated with baryta, and again filtered and evaporated, till the isethionate of baryta crystallizes. (Magnus.)—2. Ether surrounded with ice is saturated with vapour of anhydrous sulphuric acid — in which process, the formation of a certain quantity of sulphurous acid is unavoidable—the syrupy mixture evaporated with an equal bulk of ether, and then with four times its bulk of water, whereupon a solution of wine-oil produced during the process in the unaltered portion of the ether, rises to the surface. The watery liquid separated from this upper stratum is boiled for three hours, replacing the water as it evaporates, till not only the ether and sulphurous acid are volatilized, but the vinous odour is also completely dissipated; the brownish liquid is then saturated with carbonate of baryta, the filtrate evaporated till a crystalline film forms on the surface; then left to cool, whereupon crystalline flocks completely insoluble in alcohol separate out; the liquid diluted with water and filtered to separate these flocks; then evaporated to a thin syrup, and set aside to crystallize. By dissolving the resulting crystals in water, carefully precipitating with sulphuric acid, filtering, and evaporating, the aqueous acid is obtained. (Liebig.)

The acid concentrated as far as possible, is a syrup having a very sour taste. It is decomposed by further evaporation, but the dilute solution may be boiled without decomposition. (Liebig.)

The *Isethionates* crystallize readily, and sustain a heat of 200° without decomposition. According to Berzelius, their aqueous solution, when boiled with potash, neither gives off ether nor alcohol, nor produces sulphate of potash. In the dry state they are isomeric with the sulphovinates, and their crude formula is: $C^4H^5MS^2O^6$. Liebig suggests that the sulphur in isethionic acid may be in the form of hyposulphuric acid, which may be produced by the action of sulphuric acid upon ether:

$$C^4H^5O + 2SO^3 = C^4H^4O,S^2O^5 + HO.$$

This view is supported by the formation of sulphite of potash, which takes place when the potash-salt is fused with hydrate of potash; since, as found by Liebig as well as by Berzelius, sulphate of potash is not reduced to sulphite by ignition with potash and any organic substance. Since however, according to this view, an anhydrous isethionate should be $= MO, C^4H^4O, S^2O^5, = C^4H^4MS^2O^7$, whereas these salts are never actually obtained in a higher state of dryness than that which is denoted by the formula: $MO,C^4H^4O,S^2O^5 + HO = C^4H^5MS^2O^8$, we should be led to the improbable supposition that the isethionates can retain 1 At. water at 200°. Hence Berzelius proposes to regard isethionic acid as a compound of a bioxide of ethyl with hyposulphuric acid $= C^4H^5O^2,S^2O^5$, its salts would then be $= MO,C^4H^5O^2,S^2O^5 = C^4H^5MS^2O^8$. But neither Liebig's nor Berzelius' hypothesis is in accordance with the nucleus-theory, inasmuch as each of them assumes the existence of an uneven compound (C^4H^4O or $C^4H^5O^2$).

Isethionate of Ammonia. — Octohedrons which remain transparent, and do not diminish in weight either in vacuo or 120°. (Regnault.)

	Crystallized.		Regnault.
4 C	24	16·78	16·95
N	14	9·80	
9 H	9	6·29	6·40
2 O	16	11·19	
2 SO^3	80	55·94	
$NH^4O,C^4H^5O,2SO^3$	143	100·00	

Isethionate of Potash. — By saturating the acid with carbonate of potash, or precipitating the baryta-salt with carbonate or sulphate of potash. Rhombic prisms and shining laminæ, resembling chlorate of potash, which at 300° neither lose weight nor decompose. (Liebig, Regnault.) Between 300° and 350°, the salt melts, forming a transparent and colourless liquid which, on cooling, solidifies in a fibrous, porcelain-like mass of unaltered weight. (Liebig.) The salt does not give off water till it is heated to 400°, at which temperature it decomposes. (Berzelius.) The salt heated with hydrate of potash, swells up considerably, gives off hydrogen, and yields a mass containing 52·75 p. c. (1 At.) sulphate of potash, together with a certain portion of sulphite; it therefore contains sulphur in the form of hyposulphuric acid, S^2O^5, which is afterwards converted into sulphate and sulphite of potash; for hyposulphate of potash is also converted into sulphate and sulphite when heated with hydrate of potash (Liebig). 100 pts. of the salt heated with hydrate of potash, merely till the mass swells up and cakes together, yield 27·97 per cent. (somewhat more than 1 At.) of sulphuric acid in the form of sulphate of potash; but if more strongly heated till it blackens and fuses, it yields 46·25 pts. (nearly 2 At.) in the same state (Magnus, *Pogg.* 47, 516.) The salt dissolves in alcohol, especially when hot, in which case the solution deposits a considerable quantity of crystals as it cools. (Liebig.)

	Crystallized.		Liebig.	Regnault.
KO	47·2	28·75	28·49	28·20
2 SO^3	80·0	48·72		49·63
4 C	24·0	14·62	14·80	14·30
5 H	5·0	3·04	3·05	3·06
O	8·0	4·87		4·81
$C^4H^5KO^2,2SO^3$	164·2	100·00		100·00

Isethionate of Baryta. — Preparation (p. 429). — This salt crystallizes readily, especially from the alcoholic solution. (Magnus.) Small translucent laminæ. (Regnault.) The crystals neither decompose nor suffer any loss of weight at 200°. (Liebig.) At a stronger heat (above 300°, according to Regnault), the salts swells up to 100 times its bulk, blackens, and gives off a liquid having a peculiar penetrating odour, similar to that of xanthoil. (Magnus.) No sulphurous acid is evolved in this decomposition. The intumescence may be prevented by adding a few drops of oil of vitriol. (Liebig.) The salt mixed with nitre or chlorate of potash detonates violently when heated, even if the quantity of chlorate of potash be very large. It is but slowly decomposed by nitric acid, even by the fuming acid, yielding 60·46 per cent. of sulphate of baryta. It dissolves readily in water, and slowly in alcohol; more readily, however, than ethionate of baryta. (Magnus.)

	Crystallized.		Magnus.	Liebig.	Regn.	Woskresen.
BaO	76·6	39·57	39·68	39·57	39·57	39·26
$2\,SO^3$	80·0	41·32	41·56		40·60	41·12
4 C	24·0	12·40	12·13		12·37	12·47
5 H	5·0	2·58	2·62		2·62	2·61
O	8·0	4·13	4·01		4·84	4·54
$C^4H^5BaO,2SO^3$	193·6	100·00	100·00		100·00	100·00

Isethionate of Copper. — Formed from the baryta-salt and sulphate of copper. The green filtrate, evaporated to dryness and set aside in a warm place, yields sea-green, transparent, regular octohedrons, which are permanent in the air. (Liebig.) Irregular octohedrons of a very pale green colour. (Regnault.) The crystals turn white between 100° and 130°, and give off 10·5 p. c. (2 At.) of water (Liebig); they give off 10·76 p. c. at 140°. (Regnault.)

	Dehydrated.		Liebig.	Regnault.
$CuO,2SO^3$	120	76·43		
4 C	24	15·28	15·39	15·54
5 H	5	3·19	3·26	3·17
O	8	5·10		
$C^4H^5CuO^2,2SO^3$	157	100·00		

Althionic Acid. $C^4H^6O^2,2SO^3$.

REGNAULT (1837). *Ann. Chim. Phys.* 65, 98; also *Ann. Pharm.* 25, 43.

Formed when alcohol is heated with excess of oil of vitriol till olefiant gas begins to be evolved, which takes place between 160° and 180°. When equal parts of oil of vitriol and alcohol are used, nothing but sulphovinic acid is formed; and even in the residues of the ether-preparation on the large scale, the latter is the only acid found. (Regnault.) — Magnus (*Pogg.* 47, 523) was not able to find althionic acid in the residues of the preparation of olefiant gas, but only ethionic, isethionic, and sometimes also sulphovinic acid.

Preparation. The residue obtained in the preparation of olefiant gas from 6 pts. oil of vitriol and 1 pt. alcohol is saturated with milk of lime; the filtrate evaporated; the lime precipitated therefrom by oxalic acid; the filtrate saturated with baryta-water; the excess of baryta precipitated by a stream of carbonic acid gas; and the filtrate evaporated, first by heat, and finally in vacuo, whereupon crystallization takes place as soon as the liquid acquires a syrupy consistence. The crystals of althionate of baryta thus obtained are purified by recrystallization. From them may be obtained the acid (which has not been further examined) and the rest of its salts. (Regnault.)

Althionate of Ammonia. — Small deliquescent laminæ, extremely soluble in water.

Dried in vacuo.			Regnault.
4 C	24	16·78	17·75
9 H	9	6·30	6·32
N	14	9·79	
2 O	16	11·19	
2 SO^3	80	55·94	
$C^4H^5(NH^4)O^2,2SO^3$	143	100·00	

Althionate of Baryta. — Preparation. (p. 431.) — Spherules composed of small needles, permanent in the air, giving off 8·59 p. c. (2 At.) water in vacuo. The aqueous solution of the salt decomposes by continued boiling, sulphate of baryta being deposited, and the acid set free. On saturating this acid with baryta, filtering to separate the sulphate, and evaporating, a very soluble salt is obtained, probably isethionate of baryta; the isethionic acid was probably not formed during the boiling, but pre-existed in the baryta-salt used. — Althionate of baryta dissolves much more easily in water, and crystallizes much less readily than the sulphovinate; it also dissolves in alcohol, especially when hot, and more readily than the isethionate.

Dehydrated.			Regnault.
BaO	76·6	39·57	39·35
2 SO^3	80·0	41·32	41·18
4 C	24·0	12·40	12·78
5 H	5·0	2·58	2·87
O	8·0	4·13	3·82
$C^4H^5BaO^2,2SO^3$	193·6	100·00	100·00

Althionate of Lime. — The aqueous solution evaporated at the gentlest possible heat, solidifies completely in a mass, without crystallizing.

Althionate of Copper. — Pale green, very thin rhombohedrons, whose acute angle is equal to 60°. (Regnault.)

Ethionic Acid. $C^4H^6O^2,4SO^3 = 2(HO,SO^3) + C^4H^4,2SO^3$.

MAGNUS (*Pogg.* 27, 378; also *Ann. Pharm.* 6, 162. — *Pogg.* 47, 514.

Aethionsäure, Aetherschwefelsäure, Acide éthionique. — Discovered by Magnus in 1833.

Formation. — When sulphate of carbyl is dissolved in water: hence also when absolute alcohol or ether, which has absorbed the vapour of anhydrous sulphuric acid, is diluted with cold water. (Magnus.)

Preparation. — Either by dissolving pure sulphate of carbyl in water at ordinary temperatures; — or by dissolving the contents of the bottles in which sulphate of carbyl has been prepared (p. 413), consisting of sulphate of carbyl and a large quantity of anhydrous sulphuric acid, in absolute alcohol, and then mixing the solution with water; — or by passing the vapour of anhydrous sulphuric acid into absolute alcohol surrounded with ice (because if the liquid were to become hot, sulphurous acid having the odour of wine-oil would be evolved), and mixing the yellowish oil with

which process, if a sufficient excess of alcohol be present, is not attended with evolution of heat; — or by passing the vapour of anhydrous sulphuric acid into ether, whereby a similar yellowish liquid is produced; on mixing this liquid with water, any excess of ether that may be present separates out, together with sulphovinate of wine-oil, which is always formed at the same time; in the other three modes of preparation this does not take place.

On saturating either of these four aqueous mixtures, which contain ethionic acid, together with more or less sulphuric and isethionic acids, with carbonate of baryta, either in the cold or at a moderate heat; filtering from the sulphate of baryta; evaporating the filtrate over oil of vitriol, either in vacuo or in the air, at a temperature much below 100°, to such a degree that the salt begins to separate out; and then mixing the solution with a quantity of absolute alcohol, sufficient to bring the specific gravity of the mixture to 0·90, ethionate of baryta is precipitated, while the isethionate remains in solution. If too much alcohol were added, the latter salt would also be precipitated. The loosely coherent precipitate of ethionate of baryta is washed with 65 per cent. alcohol, dissolved repeatedly in water, and precipitated by absolute alcohol, to free it completely from isethionate of baryta;—then dried in vacuo; dissolved in lukewarm water, because a small quantity of alcohol, or some product of decomposition, still adheres to it; and the solution evaporated at a gentle heat, which process may however give rise to a certain amount of decomposition. (Magnus.)

From the aqueous solution of the baryta-salt, *Aqueous Ethionic acid* may be obtained by adding sulphuric acid in exact proportion, and filtering; but it cannot be concentrated without decomposing, even at ordinary temperatures, in vacuo over oil of vitriol; and at 100°, even in a state of great dilution, it is quickly resolved into sulphuric and isethionic acid. (Magnus):

$$C^4H^6O^2,4SO^3 = C^4H^6O^2,2SO^3 + 2SO^3.$$

The *Ethionates* are either uncrystallizable or crystallize with difficulty. They dissolve in water, and many of them are precipitated therefrom by alcohol. When heated, they give off empyreumatic products and sulphuric acid, and leave sulphates mixed with charcoal. (Magnus.) — In the perfectly dry state, their composition appears to be $2(MO,SO^3) + C^4H^4,2SO^3 = C^4H^4M^2O^2,4SO^3$; according to this formula, 2 At. of hydrogen in the alcohol must be replaceable by metals.

Ethionate of Ammonia. — Crystallizes readily and completely. (Magnus.)

Ethionate of Potash. — Obtained by precipitating the baryta-salt with sulphate of potash. Crystallizes very readily. The crystals do not lose weight in vacuo over oil of vitriol, or by gentle heating. When more strongly heated, they swell up considerably, still more when moistened with sulphuric acid, less with nitric acid. When the salt is heated to a certain point with excess of hydrate of potash, nearly all the sulphur that it contains is converted into sulphate of potash. If the heating be carried only so far as to cause the mass to cake together after swelling up, 1 At. of the salt yields rather more than 2 At. sulphate of potash; but if the salt be heated till it blackens and fuses, nearly 4 At. sulphate of potash are produced; a small quantity of sulphide of potassium appears, however,

to be likewise formed. In this manner, 100 pts. of the potash-salt yield, when gently heated, 32·35 parts, and when strongly heated, 53·79 pts. of sulphuric acid in the form of sulphate of potash. (Magnus.)

Crystallized.				Magnus.
2 (KO,SO^3)	174·4	....	59·85	59·70
2 SO^3	80·0	....	27·45	
4 C	24·0	....	8·24	8·45
5 H	5·0	....	1·72	1·73
O	8·0	....	2·74	
$C^4H^4K^2O^2,4SO^3+Aq$	291·4	....	100·00	

Ethionate of Soda. — Prepared in a similar manner. Beautiful crystals, which do not diminish in weight in vacuo over oil of vitriol, or when heated to 150° in the air, but begin to melt at 150°, and at a higher temperature, swell up, blacken, and ultimately decompose, with sublimation of sulphur. (Magnus.)

Crystallized.				Magnus.
2 (NaO,SO^3)	142·4	....	53·05	52·07
2 SO^3	80·0	....	29·81	
4 C	24·0	....	8·94	9·17
6 H	6·0	....	2·24	2·22
2 O	16·0	....	5·96	
$C^4H^4Na^2O^2,4SO^3+2Aq$	268·4	....	100·00	

Ethionate of Baryta. — Preparation (p.433.) — The salt, after drying in the air, does not lose weight in vacuo. It begins to decompose at 100°, giving off sulphuric acid and an empyreumatic substance having a peculiar odour, and blackening from separation of charcoal, which at a red heat converts part of the sulphate of baryta into sulphide of barium. The salt dissolves in 10 pts. of water at 20°; its dilute solution sustains a boiling heat without decomposition, but the concentrated solution decomposes even by evaporation below 100°. It dissolves very slowly in alcohol, and is precipitated by absolute alcohol from its aqueous solution. (Magnus.) — The salt, after being dried at the ordinary temperature in a current of dry air, gives off 4·2 p. c. of water in vacuo over oil of vitriol. (Marchand, *Pogg.* 32, 466.) [This is somewhat more than 1 At.; and the formula of the perfectly anhydrous salt should therefore be: $C^4H^4Ba^2O^2,4SO^3$.]

Dried in the air.				Magnus.
2 (BaO,SO^3)	233·2	....	66·59	66·48
2 SO^3	80·0	....	22·85	22·85
4 C	24·0	....	6·85	6·97
5 H	5·0	....	1·43	1·42
O	8·0	....	2·28	2·28
$C^4H^4Ba^2O^2,4SO^3+Aq$	350·2	....	100·00	100·00

Ethionate of Lime and *Ethionate of Lead* do not crystallize; their reactions are similar to those of the baryta salts. (Magnus.)

Ethionate of Copper crystallizes with difficulty. (Magnus.)

The *baryta-salt* takes the form of white crystals, which give o water at 140°; at a higher temperature they give off water, then e reumatic products containing sulphurous acid and sulphur, and sulphate of baryta mixed with charcoal. The salt fused with hydr potash yields a mixture of sulphate of baryta and sulphate of potash.

	Crystallized.			Löwig & Weidmann.
2 BaO	153·2	40·83		40·84
4 C	24·0	6·40		7·29
6 H	6·0	1·60		1·74
5 S	80·0	21·32		20·86
14 O	112·0	29·85		29·27
	375·2	100·00		100·00

Löwig (*org. Verb.* 2, 538), from an incorrect calculation, suppose salt to contain only 3 At. H; and accordingly denotes the acid, b name of *Sulfparacetylschwefelsäure.* — But the formula deducible fro preceding table is likewise improbable.

Sulphacetic Acid. $C^4H^4O^4,2SO^3$.

MELSENS (1842). *N. Ann. Chim. Phys.* 5, 392; also *Ann. Pharm* 97. — *N. Ann. Chim. Phys.* 10, 370; also *Ann. Pharm.* 52, 275 *J. pr. Chem.* 32, 71.

Essigschwefelsäure, Schwefelessigsäure, Acide Sulfacetique.

Formed by the action of anhydrous sulphuric acid on glacial acid at a gentle heat. — It is also produced, but only in small qu when glacial acetic acid is mixed with excess of fuming oil of vitri mixture being attended with evolution of heat. This mixture heated gives off nearly pure carbonic acid gas; and if the heat b tinued till the mixture turns brown, several conjugated sulphuric are also evolved; but their baryta-salts are difficult to separate.

Preparation. Vapour of anhydrous sulphuric acid is passed flask containing glacial acetic acid; the mixture heated to a certain then diluted with water, and saturated with carbonate of baryta or of lead, and the filtrate evaporated till it crystallizes.

From the lead or silver salt the acid may be separated by diss the salt in water, decomposing it by sulphuretted hydrogen, and e rating the filtrate to a syrup in vacuo. From this syrupy liquid th crystallizes in needles, or by very slow evaporation at a winter te ature, in light prisms, which are transparent and colourless. crystals fuse at about 62°, and the fused salt solidifies on cooling mass having a silky lustre. The crystals redden litmus strongly have a strongly acid taste, like that of tartaric acid, but still more — When kept for a long time in vacuo over anhydrous phosphoric they become opaque, and are reduced to $C^4H^4O^4,2SO^3+2Aq.$; the cr in their original state are composed of $C^4H^4O^4,2SO^3+3Aq.$; and the so concentrated as far as possible in vacuo, is $C^4H^4O^4,2SO^3+4Aq.$ M however, writes the formula in a different way; *e. g.* the dehyd crystals $=C^4(H^2SO^2)O^3,SO^3,2HO+2Aq.$ Berzelius halves the a

weight of the acid, and regards it, in the hypothetically anhydrous state, as *Formyloxyd-Schwefelsäure* $= C^2HO,SO^3$; therefore, when dried *per se*, as HO,C^2HO,SO^3.

The crystals, after being kept for some time at 100°, no longer crystallize, or crystallize imperfectly, on cooling; at 160°, they turn brown, and emit an odour like that of caramel; at 200°, they undergo complete decomposition, and give off an acid liquid. When burnt they leave a small quantity of charcoal, which may readily be made to burn away completely. When the dilute acid is heated for some hours to 160° in a sealed glass tube, it acquires the odour of caramel, but not the power of precipitating chloride of barium. — The acid is not decomposed by potash into sulphuric and acetic acid.

Combinations. The crystals deliquesce very rapidly when exposed to the air.

The *Sulphacetates*, in their driest state, have the composition: $C^4H^2M^2O^4,2SO^3$; — according to Melsens: $2MO,C^4(H^2SO^2)O^3,SO^3$; according to Berzelius: MO,C^2HO,SO^3. When heated, they first give off their water of crystallization, but do not melt; then evolve carbonic and sulphurous acid; and after the charcoal has burned away in the air, generally leave a residue of sulphate. They are likewise decomposed by boiling oil of vitriol, with evolution of sulphurous and carbonic acid. They appear to be all soluble in water.

Sulphacetate of Potash. — Separates from the hot aqueous solution in small crystals containing $C^4H^2K^2O^4,2SO^3+2Aq$.

Sulphacetate of Baryta. — Crystalline crust, consisting of small opaque laminæ, which give off their water of crystallization between 250° and 260°, and at a higher temperature decompose with intumescence, and leave a residue of sulphate of baryta. This salt dissolves slowly in water, more slowly when dehydrated than in the hydrated state; hence the free acid added to concentrated solutions of other baryta-salts, throws down needles; water containing hydrochloric acid dissolves it in greater quantity.

Dried at 250°.			Melsens.
2 BaO	153·2	55·67	55·65
4 C	24·0	8·72	8·42
2 H	2·0	0·72	0·79
2 S	32·0	11·63	12·29
8 O	64·0	23·26	22·85
$C^4H^2Ba^2O^4,2SO^3$	275·2	100·00	100·00

Crystallized.			Melsens.
2 BaO	153·2	50·69	50·67
4 C	24·0	7·94	8·07
5 H	5·0	1·66	1·61
2 S	32·0	10·59	10·48
11 O	88·0	29·12	29·17
$C^4H^2Ba^2O^4,2SO^3+3Aq$	302·2	100·00	100·00

The crystals give off 8·58 p. c. water at 250°. There are other crystals containing 1 At. water less $= C^4H^2Ba^2O^4,2SO^3+2Aq$.

Sulphacetate of Lead. — Small, transparent needles, permanent in the air, sometimes united in tufts, sometimes in opaque nodules. Decomposes between 200° and 210°.

Crystallized.			Melsens.
2 PbO	224	61·53	61·26
4 C	24	6·60	6·57
4 H	4	1·10	1·27
2 S	32	8·79	
10 O	80	21·98	
$C^4H^2Pb^2O^4,2SO^3+2Aq$	364	100·00	

Sulphacetate of Silver. — Formed by precipitating the aqueous solution of the baryta-salt with sulphuric acid; digesting the filtrate with carbonate of lead to remove the excess of sulphuric acid; removing the lead from the filtrate by sulphuretted hydrogen; boiling the filtrate till all the excess of the gas is expelled, and saturating it with oxide of silver; then evaporating, and leaving the solution to crystallize by cooling. If too much oxide of silver be added, the solution becomes alkaline, and the crystals which it yields are contaminated with a black powder. — Long, flat, transparent prisms, with dihedral summits. They blacken slowly in daylight. In vacuo over oil of vitriol, or at 100° in a current of air, they become opaque and give off 5 p. c. (2 At.) of water. At higher temperatures, they fuse and swell up, emitting an odour of acetic and sulphurous acid, and leaving metallic silver. — The dehydrated salt is $C^4H^2Ag^2O^4,2SO^3$; the crystallized salt contains 2 At. water in addition. (Melsens.)

If from the solution of the silver-salt in absolute alcohol, the silver be precipitated as chloride by dry hydrochloric acid gas, and the filtrate left to evaporate in vacuo over oil of vitriol and lime (to absorb the hydrochloric acid), a new acid, *Sulphacetovinic acid*, remains in the form of a syrup. This acid dissolves in water, reddens litmus, effervesces even in the cold with carbonates, and does not precipitate baryta or silver salts. On saturating it at a gentle heat with oxide of silver, evaporating the solution in vacuo, and removing the crystals of sulphacetate of silver which separate out at first, — the remaining liquid, when strongly concentrated, solidifies in a nodular, unctuous, slowly deliquescent mass, which may be freed from adhering mother-liquor by pressure between paper. This new silver-salt crystallizes in nacreous laminæ from a boiling solution in absolute alcohol. It blackens slowly in daylight. At 100°, it melts to a colourless liquid, and on cooling, solidifies in a mass having a pearly lustre. But when kept for some time at 100°, the salt decomposes to a slight extent, with partial solidification (but without perceptible blackening), the relative quantities of C and H diminishing, while that of Ag increases. About 100°, the salt boils, swells up, gives off combustible gases which burn with a smoky flame, and leaves silver. (Melsens.)

According to Melsens, this acid may be regarded as $C^4(H^2SO^2)O^2$, $C^4H^5O,HO[=C^4H^6O,C^4H^3O^3,SO^3]$; but if this formula be admitted, we cannot very well see what becomes of the second atom of sulphuric acid in the sulphacetic acid. According to its mode of formation, this acid may perhaps be regarded as a conjugated compound of acetic ether with sulphuric acid: $C^4H^2Ag^2O^4,2SO^3+C^4H^8O^2+2HCl=C^8H^8O^4,2SO^3+2HO+2AgCl$.

Oxysulphocarbonate of Ethyl, or Xanthic Ether.

$C^6H^5OS^2 = C^4H^5O,CS^2$.

ZEISE (1845.) *Ann. Pharm.* 55, 304; also *J. pr. Chem.* 36, 352.
DEBUS. *Ann. Pharm.* 75, 121; abstr. *Pharm. Centr.* 1851, 225; *Laur. & Gerh. C. R.* 1850, 408; *Jahresber.* 1850, 463.

Schwefelkohlenstoffäther, Aethyloxydschwefelkohlenstoff, Aethyloxydsulfocarbonat, Schwefelkohlenstoffvinester, xanthonsaures Aethyloxyd, Ether sulfocarbonique, Ether xanthique.

Formation.—1. By the action of iodine on xanthate of potash:

$$C^4H^5KO^2,2CS^2 + I = C^4H^5O,CS^2 + KI + 2S + C + O.$$

The sulphur is precipitated; the 1 At. C and 1 At. O probably combine with 1 At. I, forming a compound resembling phosgene. (Zeise.) At first, $C^4H^5KO^2,2CS^2 + I$ forms $KI + C^4H^5O^2,2CS^2$; but this compound is decomposed by distillation, with formation of xanthic ether. (Desains, *vid.* p. 441.)—¶ 2. By the action of chloride of ethyl on xanthate of potash. (Debus.)

$$C^4H^5KO^2,2CS^2 + C^4H^5Cl = KCl + 2(C^4H^5O,CS^2).$$

3. In the destructive distillation of bioxysulphocarbonate of ethyl xanthic ether is given off between 200° and 210°. (Desains, Debus, pp. 442, 443.)

Preparation. Xanthate of potash is made up into a paste with absolute alcohol, and finely pulverized iodine added in small portions and with constant stirring, till the light yellow liquid above the iodide of potassium and the precipitated sulphur produced by the action, begins to turn brown from excess of iodine,—after which more xanthate of potash is added, with agitation, in quantity just sufficient to remove the excess of iodine. So long as any excess of iodine is present, the addition of water to a filtered sample of the liquid causes the separation of the brown oil, and the mixture colours starch blue; but after the excess of iodine has been removed, the oil separated by water has a light yellow colour, and no bluing of starch takes place.—When the right proportion has been found, the mixture is set aside for 24 hours in a stoppered bottle, whereupon more iodide of potassium and sulphur is deposited; the deposit is collected on a filter, washed with alcohol, and the whole of the filtrate distilled till the residue is reduced to one-fourth.

If the distillate thus obtained be again distilled down to one-sixth, the residue forms with water a milky liquid, from which xanthic ether separates; and the $\frac{5}{6}$ distillate mixed with water also becomes milky and deposits a white powder, together with a pale yellow oil, which has an odour different from that of xanthic ether, is very inflammable, burns with a pale blue flame, and leaves a brown, tarry residue which colours starch blue. This oil perhaps contains the 1 At. C and O of the above equation.

The residue left after distilling to one-fourth, deposits sulphur and a small quantity of iodide of potassium on cooling. The clear liquid is decanted; the deposit thrown on a filter and washed with a small quantity

of alcohol; the entire liquid distilled at an increasing heat; the receiver changed at 150°; and the remaining liquid distilled nearly to dryness. There then remains a tolerably large quantity of a black varnish-like mass, which is perhaps only a secondary product; it blues starch-paste on the addition of nitric acid; yields sulphur and a carbonaceous mass when heated; and dissolves for the most part in water, forming a brown-black, alkaline liquid.

The distillate obtained above 150°, which forms a light yellow oil whose boiling point continually rises, is freed from alcohol by agitation with a four or five-fold quantity of water, and from the upper watery layer by means of a separating funnel. — If the receiver has been changed below 150°, the oil contains so much alcohol, that when mixed with water, it forms a milky liquid from which only a very small quantity of oil separates. The oil is shaken up with 4 or 5 pts. of fresh water, then carefully separated from the water, set aside for 24 hours in contact with coarsely pounded chloride of calcium, then filtered and again distilled to dryness, after which it exhibits a constant boiling point of 220°, and passes over as pure xanthic ether, leaving behind a few brownish spots. (Zeise.)

¶ An alcoholic solution of xanthate of potash is mixed with an equivalent quantity of hydrochloric ether; the liquid left to itself for 5 or 6 days at a temperature between 12° and 18°, then mixed with twice its volume of water to dissolve the chloride of potassium and separate the xanthic ether; and the latter purified by washing with water, drying over chloride of calcium, and rectification. (Debus.) ¶

Properties. Clear, light yellow oil of sp. gr. 1·0703 at 18° (Zeise); 1·07 (Debus). Does not solidify at −20°. Boils at 212° [it is stated at 220° above] (Zeise); at 200° (Debus). Has a tolerably strong and somewhat unpleasant odour, a sweetish taste, and is neutral to vegetable colours. (Zeise.)

			Zeise.	Debus.
5 C	30	40·00	39·61	39·45
5 H	5	6·67	6·63	6·38
2 S	32	42·67	43·03	
O	8	10·66	10·73	
C^4H^5O,CS^2	75	100·00	100·00	

Decompositions. 1. Xanthic ether takes fire in the air, but only when strongly heated; it then burns away, forming sulphurous acid. — 2. With strong *Nitric acid* it mixes quietly at first, but after a few seconds, violent action takes place. — ¶ 3. *Sulphuric acid* mixes with xanthic ether, giving off sulphurous acid, and separating an oily body, the quantity of which may be increased by diluting the liquid with water. — A mixture of sulphuric and fuming nitric acid acts very strongly on xanthic ether, evolving nitrous acid. When the decomposition is at an end, and all the xanthic ether is dissolved, a yellow oil separates out on diluting the liquid with water. — Hydrochloric acid has no action on xanthic ether. ¶ — 4. A solution of xanthic ether in absolute alcohol containing *hydrate of potash*, set aside in a closed vessel, solidifies in 6 or 8 hours, by formation of a crystalline powder consisting of pure carbonate of potash, and the mixture acquires the odour of mercaptan, which compound may be separated by filtering from the crystalline powder, mixing the filtrate with alcohol, and distilling:

$$C^5H^5S^2O + HO,KO = C^4H^6S^2 + KO,CO^2.$$

If however the above mixture of xanthic ether and alcoholic potash be set aside for a longer time, or if it be heated, further decompositions take place, resulting in the formation of xanthate of potash and sulphide of potassium.

¶ According to Debus (*Ann. Pharm.* 75, 128), xanthic ether dissolved in the smallest possible quantity of alcohol, and mixed with twice its weight of hydrate of potash in the state of concentrated alcoholic solution, deposits, when left to itself at 0°, crystals of *oxyxanthate of potassium*, $C^4H^5KS^2,CO^2$ (p. 461), while mercaptan remains in solution:

$$2(C^4H^5O,CS^2) + KO,HO = C^4H^5KS^2,2CO^2 + C^4H^6S^2.$$

5. An alcoholic solution of xanthic ether mixed with a similar solution of *sulphide of hydrogen and potassium* solidifies in a few days, forming a magma of xanthate of potash, mercaptan being produced at the same time. (Debus):

$$2(C^4H^5O,CS^2) + KS,HS = C^4H^5KO^2,2CS^2 + C^4H^6S^2.$$

6. Xanthic ether is not altered by immersion in aqueous *ammonia;* but when dry ammonical gas is passed into the alcoholic solution of the ether, complete decomposition takes place after a while; the liquid which passes over, on distilling the mixture, contains sulphide of ammonium and sulphide of ethyl, while *xanthamide* (vid. p. 443) remains in solution. (Debus):

$$2(C^4H^5O,CS^2) + 2NH^3 = \underbrace{C^6H^7NS^2O^2}_{\text{Xanthamide.}} + NH^4S + C^4H^5S.$$

7. Protochloride of mercury added to an alcoholic solution of xanthic ether forms a white precipitate. — Protoxide of mercury, peroxide of lead, and protoxide of lead, produce no action, even with the aid of heat. Chloride of calcium, protochloride of copper, and nitrate of silver, are likewise without action on an alcoholic solution of xanthic ether. ¶ — 8. Potassium and sodium do not act on xanthic ether in the cold, and even on the application of heat, only a small quantity of gas is evolved.

Combinations. Xanthic ether is quite insoluble in water.
It dissolves *Iodine*, forming a brown transparent oil.
It mixes in all proportions with *Alcohol* and *Ether*.

Bioxysulphocarbonate of Ethyl.

$$C^6H^5S^4O^2 = C^4H^5O^2,C^2S^4 = C^4H^5O,C^2S^4O.$$

DESAINS. *N. Ann. Chim. Phys.* 20, 469; abstr. *Compt. rend.* 23, 1089.
DEBUS. *Ann. Pharm.* 72, 1; abstr. *Pharm. Centr.* 1850, 117, 135; *Laur. & Gerh. C. R.* 1850, 50; *Chem. Gaz.* 1850, 143; *Jahresber.* 1849, 419.

When iodine extracts the potassium from xanthate of potash, $C^4H^5KO^2,2CS^2$, this compound remains behind. (Desains.) — ¶ Similarly with xanthate of lead. (Debus.)

According to Debus, it is probable that when protochloride of copper is heated with xanthate of potash (a process whose ultimate product was regarded by Zeise as a

body having the composition of xanthic ether), a compound isomeric with bioxysulphocarbonate of ethyl is formed; for if after the alcoholic solution of xanthate of potash has been treated with protochloride of copper, the liquid be separated by filtration from the cuprous xanthate thereby formed, and the filtrate mixed with water, an oily body is precipitated, which, though it does not crystallize even when its alcoholic solution is cooled to 0°, nevertheless agrees in its other properties with bioxysulphocarbonate of ethyl. ¶

Preparation. 1. Iodine is added to an alcoholic solution of xanthate of potash, so long as it does not colour the liquid permanently, and the mixture is left to evaporate spontaneously in the air; it then, after a few days, deposits crystalline laminæ, which may be freed from iodide of potassium by washing with water. The compound is likewise precipitated in the form of a white powder when alcoholic tincture of iodine is mixed at ordinary temperatures with aqueous xanthate of potash, in such proportion as to decolorize the tincture. In summer the compound can only be obtained in the form of an oil, which must be washed with water, and dried over chloride of calcium. (Desains.) — ¶ According to Debus, the alcoholic solution of xanthate of potash, after being treated with iodine, may be immediately diluted with water, and left to itself at 12°. If a concentrated alcoholic solution of xanthate of potash be used, the compound separates, on diluting the liquid with water, in the form of a yellow oil, which in the course of a few hours solidifies in the form of a crystalline mass. — 2. The compound may also be obtained by treating xanthate of lead suspended in water with iodine, till the liquid assumes a permanent brown tint, adding more xanthate of lead to remove the excess of iodine, mixing the clear colourless filtrate with an equal bulk of water, and leaving it to itself for 10 or 12 hours at about 12°; the compound then crystallizes in small white prisms, which are easily freed from adhering iodide of lead by recrystallization. (Debus.)

Properties. Bioxysulphocarbonate of ethyl crystallizes from dilute solutions in concentric groups of white shining prisms reduced to tables. At 28° (or at the heat of the hand, according to Desains) it fuses to a yellowish oil, which has a peculiar odour (persistent, but not unpleasant: according to Desains), and crystallizes again but slowly. After being heated to 100°....120° the liquid does not crystallize any more on cooling. (The compound may also be at once obtained in the form of an uncrystallizable liquid, if the temperature be raised too high during its preparation by a too rapid addition of iodine.) At 160°, decomposition takes place. The compound dissolves readily in absolute alcohol and in ether. (Debus.) ¶

				Desains.	Debus.
6 C	36		29·75	29·1	29·77
5 H	5		4·13	4·2	4·23
4 S	64		52·90	53·5	53·50
2 O	16		13·22	13·2	12·50
$C^6H^5S^4O^2$	121		100·00	100·0	100·00

Decompositions. Between 200° and 210°, only a small portion of the compound distils over unaltered, the greater part being resolved into sulphocarbonate of ethyl, carbonic acid and carbonic oxide gases, vapour of sulphide of carbon, and a residue of sulphur. Equation, when carbonic acid is produced:

$$2C^6H^5S^4O^2 = 2C^3H^5S^2O + CO^2 + CS^2 + 2S;$$

Equation, when carbonic oxide is formed:

$$C^6H^5S^4O^2 = C^5H^5S^2O + CO + 2S.$$

Carbonic acid and carbonic oxide are always evolved together, the carbonic acid predominating. The residual sulphur has a blackish tint, arising from the presence of a small quantity of carbonaceous matter. As the sulphocarbonate of ethyl which passes over is still contaminated with a portion of the undecomposed compound, its analysis gives 37·7 p. c. carbon and 6·1 hydrogen; but after the compound $C^6H^5S^2O^4$ has been removed by a second distillation, the sulphocarbonate of ethyl gives by analysis 36·9 C and 6·6 H. (Desains.) — ¶ Bioxysulphocarbonate of ethyl, subjected to dry distillation, begins to decompose at 130°; and at 170°, the decomposition is so rapid that the distillation may be terminated without further application of heat from without. The gas evolved in the decomposition is carbonic oxide mixed with small quantities of carbonic acid and sulphide of carbon. The residue consists of sulphur. The boiling point of the distillate varies from 50° to 210°. When it was heated for some time to 50°, a small quantity of sulphide of carbon was given off from it; on raising the heat to 140°, scarcely anything passed over; between 175° and 190°, principally *carbonate of sulphethyl* (p. 445):

$$C^6H^5S^4O^2 = CS^2 + S + C^4H^5S,CO^2.$$

between 190° and 200°, but a small quantity of distillate was obtained; between 200° and 210°, xanthic ether (Debus). ¶ — Oil of vitriol decomposes the compound, even at ordinary temperatures, giving off a large quantity of sulphurous acid; but hydrochloric acid may be distilled over it without alteration. (Desains.) — Absolute alcohol saturated with dry ammoniacal gas separates sulphur from the compound, and forms a brown-red solution, which, when evaporated in vacuo, solidifies in semicrystalline crusts containing 30·97 p. c. C, 6·6 H, and 14·0 N. Ether dissolves a portion of these crusts, leaving undissolved a quantity of white crystals containing 16·8 p. c. C and 5·8 H. The ethereal solution, when evaporated, yields large flexible needles of another substance, containing 34·0 p. c. C and 7·0 H. (Desains.) — ¶ When dry ammoniacal gas is passed into an alcoholic solution of bioxysulphocarbonate of ethyl, the liquid soon rises in temperature and becomes turbid, from deposition of sulphur; and if the passage of the gas be discontinued as soon as the separation of sulphur is at an end, the liquid then filtered, and the filtrate evaporated to dryness in vacuo, an efflorescent residue is obtained, consisting of small aggregated needles of xanthate of ammonia, saturated with an oily body, which is *Xanthamide*:

$$2C^6H^5S^4O^2 + 2NH^3 = 2S + \underbrace{C^4H^5(NH^4)O^2,2CS^2}_{\text{Xanthate of ammonia.}} + \underbrace{C^6H^7NS^2O^2}_{\text{Xanthamide.}}.$$

The xanthamide may be dissolved out by ether; and on evaporating the ether, it remains in the form of an oil having an alliaceous odour, and gradually solidifying when cooled below 28°. — Dry ammoniacal gas passed over dry bioxysulphocarbonate of ethyl at about 70°, yields volatile products consisting of sulphide of carbon, sulphocarbonate, sulphocyanide, and sulphide of ammonium, and a residue consisting of xanthamide, sulphur, and the greater part of the sulphocyanide of ammonium. (Debus.) — When an alcoholic solution of bioxysulphocarbonate of ethyl is mixed with an alcoholic solution of hydrate of potash, sulphur separates out, and a solution is formed containing xanthate of potash, which, by filtration,

concentration in vacuo, and cooling down to 0°, is obtained in the crystalline state, and when purified by solution in alcohol, leaves a residue of carbovinate of potash. The decomposition is represented by the following equation:

$$4C^6H^5S^4O^2 + 4KO = 3(\underbrace{C^4H^5KO^2,2CS^2}_{\text{Xanthate of potash.}}) + \underbrace{C^4H^5KO^2,2CO^2}_{\text{Carbovinate of potash.}} + 4S.$$

The carbovinate of potash is resolved into alcohol [ether ?] and carbonate of potash; part of the sulphur separates in the free state, and the rest is converted by the potash into sulphide of potassium, and probably also into hyposulphite of potash. (Debus.) Desains had previously observed that potash added to an alcoholic solution of $C^6H^5S^4O^2$, throws down sulphur and forms xanthate of potash. — When a saturated alcoholic solution of bioxysulphocarbonate of ethyl is mixed with sulphide of hydrogen and potassium, sulphuretted hydrogen is given off, sulphur is precipitated, and xanthate of potash remains in solution. (Debus.)

$$C^6H^5S^4O^2 + KS,HS = C^4H^5KO^2,2CS^2 + S + HS. \quad ¶$$

Xanthomethylate of potash treated with a solution of iodine in wood-spirit likewise yields an oil $= C^4H^3S^4O^2$, which is converted by distillation into the compound C^2H^3O,CS^2, described by Cahours (VII. 393).

¶ Vinomethylic Oxysulphocarbonate.

$$C^8H^8O^2S^4 = C^2H^3O,C^4H^5O,2CS^2 = C^2H^3O,CS^2 + C^4H^5O,CS^2.$$

CHANCEL. *Laur & Gerh. C. R.* 1850, 403; *Jahresber.* 1850, 469. — Further: *Compt. rend.* 32, 587; *Instit.* 1851, 130; *J. pr. Chem.* 53, 111; *Jahresber.* 1851, 512.

Carbométhylovinide bisulfuré, zweifach-geschwefeltes Carbomethylovinid.

Formed by distilling xanthate of potash with an equivalent quantity of sulphomethylate of potash:

$$C^4H^5KO^2,2CS^2 + C^2H^3KO^2,2SO^3 = C^4H^5O,C^2H^3O,2CS^2 + 2(KO,SO^3).$$

Pale yellow, transparent liquid, of sweet taste, and strong, ethereal, but not unpleasant odour. Sp. gr. 1·123 at 11°. Boils at 179° without decomposition. Vapour-density 4·652.

				Chancel.
8 C	48	....	35·29	..... 35·7
8 H	8	....	5·88	..... 6·0
2 O	16	....	11·77	
4 S	64	....	47·06	
$C^2H^3O,C^4H^5O,2CS^2$	136	....	100·00	

	Vol.		Density.
C-vapour	8	....	3·3280
H-gas	8	....	0·5544
O-gas	1	....	1·1093
S-vapour	$\frac{3}{2}$	....	4·4372
Vapour of $C^8H^8S^2O^4$	1	....	9·4289
	2	....	4·7144

This compound may be regarded as vinomethylic carbonate $C^2H^3O, C^4H^5O,2CO^2$, in which 4O are replaced by 4S; — also as *xanthate of methyl*, $C^4H^5MeO^2,2CS^2$, or *xanthomethylate of ethyl*, $C^2H^3AeO^2,2CS^2$.

Very inflammable and burns with a blue flame, giving off large quantities of sulphurous acid. — Ammonia decomposes it, forming xanthamide and methylic mercaptan (VII, 284):

$$C^8H^8O^2S^4 + NH^3 = C^6H^7NO^2S^2 + C^2H^4S^2.$$

This decomposition is analogous to that of vinomethylic carbonate by ammonia, the products of which are urethane and methylic alcohol: $[C^8H^8O^6 + NH^3 = C^6H^7NO^4 + C^2H^4O^2]$. Xanthamide may in fact be regarded as bisulphuretted urethane, or urethane in which 2O are replaced by 2S.

Vinomethylic sulphocarbonate is insoluble in water, but soluble in alcohol and ether. (Chancel.)

¶ Carbonate of Sulphethyl. C^4H^5S,CO^2.

DEBUS. *Ann. Pharm.* 75, 136; abstr. *Jahresber.* 1840, 465.

Obtained, together with xanthic ether and free sulphide of carbon, in the dry distillation of bioxysulphocarbonate of ethyl (p. 443); — also by decomposing oxyxanthate of potassium (p. 461), with chloride of ethyl:

$$C^4H^5S,KS,2CO^2 + C^4H^5Cl = KCl + 2(C^4H^5S,CO^2).$$

This latter reaction, however, yields but small quantities of the compound; for it takes place very slowly, and in the meanwhile the potassium-salt is for the most part converted into carbonate of potash, sulphuretted hydrogen and alcohol [by the action of atmospheric moisture?].

Colourless liquid having an agreeable ethereal odour. Sp. gr. 1·032 at 1°. Boils at 161°–162°. Insoluble in water; but easily soluble in alcohol and ether.

			Debus.
5 C	30	44·77	44·21
5 H	5	7·46	7·61
S	16	23·89	24·71
2 O	16	23·88	
C^4H^5S,CO^2	67	100·00	

Carbonate of sulphethyl is not acted upon by hydrochloric acid. Sulphuric acid acts upon it only when heated; nitric acid, only when strong and with the aid of heat. — With an alcoholic solution of sulphide of hydrogen and potassium, it forms oxyxanthate of potassium, $C^4H^5KS^2, 2CO^2$, and mercaptan:

$$2(C^4H^5S,CO^2) + KS,HS = C^4H^5KS^2,2CO^2 + C^4H^6S^2.$$

With an alcoholic solution of hydrate of potash, it yields the same products together with sulphide of potassium. — When the mixture of the two liquids is set aside in a cool place, at a temperature of about 5°, it solidifies after awhile, if sufficiently concentrated, to a crystalline mass consisting of $C^4H^5KS^2,2CO^2$. At the bottom of the vessel there also collects a clear, oily stratum containing well formed rhombic tables; this oily liquid is a concentrated solution of carbonate of potash containing crystals of the salt. The mother-liquid contains mercaptan and sulphide

of potassium. The hydrate of potash first acts on the carbonate of ethylic sulphide, forming sulphide of hydrogen and potassium, carbonate of potash, and alcohol:

$$2(C^4H^5S,CO^2) + 3(KO,HO) = KS,HS + 2C^4H^6O^2 + 2(KO,CO^2);$$

and the sulphide of hydrogen and potassium then acts on another portion of carbonate of sulphethyl in the manner above described. — When dry ammoniacal gas is passed into the alcoholic solution of carbonate of sulphethyl, decomposition takes place; the liquid acquires the odour of sulphide of ammonium, and when evaporated to the crystallizing point, yields a salt in long, yellow needles, mixed with a colourless gelatinous substance resembling precipitated silica. — Both these bodies dissolve readily in water and alcohol, and cannot be separated by crystallization; their aqueous solution forms black precipitates with lead, copper, and mercury salts. — Carbonate of ethylic sulphide may be boiled with mercuric oxide without decomposing.

¶ Bicarbonate of Bisulphethyl. $C^6H^5S^2O^4 = C^4H^5S^2,2CO^2$.

DEBUS. *Ann. Pharm.* 75, 142; *Jahresber.* 1850, 466. — Further: *Ann. Pharm.* 82, 253; *Jahresber.* 1852, 563.

Formed by the action of iodine on oxyxanthate of potassium:

$$C^4H^5S,KS,2CO^2 + I = KI + C^4H^5S^2,2CO^2.$$

Preparation. Iodine is added to an alcoholic solution of $C^4H^5KS^2$, $2CO^2$, till the liquid exhibits a brown colour; after which the excess of iodine is removed by adding a little more of the potassium-salt. The liquid is then diluted with twice its bulk of water, whereupon the compound $C^4H^5S^2,2CO^2$ separates in the form of a colourless oil, which must be washed several times with water and then dried in vacuo. The mother-liquor contains nothing but iodide of potassium.

Properties. Colourless, strongly refractive, oily liquid, which makes greasy spots on paper. It is heavier than water.

			Debus.	
6 C	24	34·28	34·67	34·73
5 H	5	4·76	4·70	4·71
2 S	32	30·48		
4 O	32	30·48		
$C^6H^5S^2O^4$	93	100·00		

Decompositions. 1. This compound heated in a tube, first gives off gas-bubbles and an ethereal substance having an agreeable odour; then becomes gradually more viscid, acquires a deep yellow colour, and gives off a pungent vapour. On cooling, nearly the whole residue solidifies in a sulphur-yellow, amorphous mass. — 2. Sulphuric and nitric acid mix with the compound at ordinary temperatures without decomposing it, decomposition not taking place till the liquid is boiled. — 3. Potash acts upon the alcoholic solution of this compound in the same manner as on

bioxysulphocarbonate of ethyl, forming oxyxanthate of potassium, $C^4H^5KS^2,2CO^2$, sulphide of potassium, and free sulphur. — Protochloride of mercury, bichloride of platinum, and acetate of lead form no precipitates with it. — 4. Strong ammonia poured upon the compound decomposes it immediately, with separation of sulphur. The liquid filtered from the sulphur, after sufficient addition of ammonia, if concentrated over the water bath and then over sulphuric acid, yields almost simultaneously, crystals of two or three different substances, and a white flocculent body, which have not yet been satisfactorily investigated. (One of the above-mentioned substances exhibited the form and characters of urethane; another, which crystallizes in prisms; dissolved readily in water and in alcohol; had a neutral reaction; was not altered by chloride of platinum, sulphate of copper, or acetate of lead; did not give off ammonia when treated with potash; fused when heated; and was afterwards resolved into a volatile liquid and a white, solid, sublimable body.)— When ammoniacal gas is passed into the alcoholic solution of $C^6H^5S^2O^4$, similar crystallizable products of decomposition are formed in small quantity. Debus regards it as probable that in these decompositions, *i.e.*, in presence of water, the compound $C^6H^5S^2O^4$ is for the most part resolved into alcohol, carbonic acid, and sulphur. — When dry ammoniacal gas was passed into a solution of the compound dissolved in a four or fivefold quantity of ether, the liquid rose in temperature and suddenly became turbid, the odour of ammonia disappearing and sulphur being separated; and this action was repeated several times. On filtering the liquid after the decomposition was completed, and expelling the ether, ammonia, and sulphide of ammonium, by heating it to 100°, a yellow oil and small white crystals separated out; the former dissolved readily in ether, the latter with difficulty. The crystals, when purified by recrystallization from boiling alcohol, proved to be the *allophanate of ethyl* $C^6H^8N^2O^5 = C^4H^5O,C^4H^3N^2O^5$, discovered by Liebig and Wöhler. (*Ann. Pharm.* 59, 291.) The mother-liquor still contained a neutral body which crystallized in needles, and an amorphous body. The yellow oil easily soluble in ether had an unpleasant odour, was heavier than water, sparingly soluble in alcohol, insoluble in water, had a neutral reaction, and gave by distillation a volatile stinking oil, while sulphur was separated and a black carbonaceous mass remained behind. Debus regards this oil as a sulphide of ethyl. For the decomposition of the compound $C^6H^5S^2O^4$ in the state of ethereal solution by ammonia, he gives the following equation:

$$2C^6H^5S^2O^4 + 2NH^3 = \underbrace{C^6H^3N^2O^6}_{\text{Allophanic ether.}} + C^4H^5S + 2S + HS + 2O.$$

Combinations. Bicarbonate of bisulphethyl is insoluble in water, but is readily dissolved by alcohol and ether. Its solubility in alcohol diminishes with the proportion of water contained in the alcohol; absolute alcohol mixes with it in nearly all proportions; but spirit of 40 per cent. takes up but small quantities of it. (Debus.)

Bicarbonate of Bisulphethyl with Bicarbonate of Sulphethyl. $C^4H^5S^2$, $2CO^2 + C^4H^5S,2CO^2 = C^{12}H^{10}S^3O^8$. — Formed by the decomposition of oxyxanthate of copper (*vid.* p. 464);

$$5(C^4H^5CuS^2,2CO^2) = [3(C^4H^5CuS^2,2CO^2) + Cu^2S] + C^{12}H^{10}S^3O^8.$$

By collecting the unctuous mass produced by this decomposition on a filter, washing it with water, then dissolving in cold alcohol, evaporating the filtered alcoholic solution in vacuo, digesting the dry residue in ether, and leaving the ethereal solution to evaporate in the air at ordinary temperatures, the compound $C^{12}H^{10}S^3O^6$ is obtained in the form of an oil, having a faint yellowish green colour, arising from a small quantity of the copper-compound $3(C^4H^5CuS^2,2CO^2) + Cu^2S$, which, not being quite insoluble in ether, becomes mixed with it. This impurity is easily removed by agitation with dilute hydrochloric acid. — The compound, after being washed in water and dried in vacuo, forms a colourless, strongly refracting liquid, which cannot be distilled, because it is resolved by heat into other ethereal compounds and a yellow crystalline substance, probably sulphur. — Heated with alcoholic potash, it yields sulphur, carbonate of potash, and a salt, which from its physical and chemical properties, appears to be oxyxanthate of potash (p. 461). Hydrochloric acid exerts no action on the compound. Nitric acid does not affect it at ordinary temperatures; but, on the application of heat, decomposes it, with evolution of nitric acid. (Debus.)

				Debus.
12 C	72	37·11	36·98	
10 H	10	5·15	5·17	
3 S	48	24·75	27·95	25·28
8 O	64	32·99		
$C^4H^5S^2,2CO^2 + C^4H^5S,2CO^2$	194	100·00		

Might also be regarded as a quadrocarbonate of sesquisulphethyl: $(C^4H^5)^3S^2,4CO^2$. ¶.

Xanthic Acid. $C^4H^6O^2,2CS^2$.

ZEISE. *Schw.* 36, 1; 43, 160. — *Pogg.* 35, 457.
COUERBE. *Ann. Chim. Phys.* 61, 225; abstr. *J. pr. Chem.* 23, 83. — *Ann. Chim. Phys.* 68, 170. — *Rev. scientif.* 3, 11; also *J. pr. Chem.* 23, 94.

Xanthonsäure, Xanthogensäure, Xanthinsäure (from its property of forming yellow precipitates with copper salts), *Acide xanthique, sulphocarbonique, sulfocarbéthénique.* Discovered and examined by Zeise in 1822.

Formation. — Sulphide of carbon, mixed with alcohol and potash, forms water and xanthate of potash:

$$KO + C^4H^6O^2 + 2CS^2 = C^4H^5KO^2,2CS^2 + HO.$$

When this salt is decomposed by an aqueous acid, xanthic acid separates out. (Zeise.)

$$C^4H^5KO^2,C^2S^4 + HO,SO^3 = KO,SO^3 + C^4H^6O^2,C^2S^4.$$

Preparation. Xanthate of potash is placed in a glass cylinder, cooled to 0° from without, and a mixture of 1 pt. oil of vitriol and 5 pts. water (hydrochloric acid may also be used,) is poured upon it till the acid is sensibly in excess; the mixture is then shaken up a little, the milky liquid mixed a few seconds afterwards with an equal bulk of water, and

then with a much larger quantity. Too much water, however, exerts a decomposing action on the finer and still disunited particles of the acid. — As soon as the oily xanthic acid has settled down, and the watery liquid has become clear, the latter is decanted from the oil by means of a pipette, and fresh water repeatedly poured on the oily acid and off again, till it no longer forms a cloud with chloride of barium. Lastly, the remaining portion of water, which would exert a decomposing action, is removed, first by the separating funnel, and then by placing the acid over chloride of calcium; and the acid is preserved in a well stoppered bottle, placed in a very cool situation. (Zeise.)

Properties. Transparent, nearly colourless oil; heavier than water; very volatile. Reddens litmus paper distinctly, but the red tint quickly changes to yellowish white. Has a strong and peculiar odour like that of sulphurous acid; its taste is astringent and somewhat acid at first, but afterwards becomes somewhat bitter and burning. — Very inflammable; precipitates copper-salts yellow. (Zeise.)

Calculation, according to Zeise.

6 C	36	29·51
6 H	6	4·92
4 S	64	52·46
2 O	16	13·11
$C^4H^6O^2,C^2S^4$	122	100·00

Therefore, 1 At. alcohol + 2 At. sulphide of carbon, or 1 At. water, 1 At. ether, and 2 At. sulphide of carbon = $HO,CS^2 + C^4H^5O,CS^2$. Xanthic acid is carbovinic acid (p. 394), in which the oxygen of the carbonic acid is replaced by sulphur.

Decompositions. 1. The acid, whether moist or perfectly dry, is resolved at a moderate heat, even at 24°, into alcohol and sulphide of carbon; at the same time, it becomes heated and disturbed, even to slight tumefaction. If the acid contained in a retort be then gradually heated to 50°, then to 70°, and lastly to 90°, the first distillate, which passes over spontaneously, contains scarcely anything but sulphide of carbon; the second, the same substance with a little alcohol; the third, a large quantity of alcohol with a little sulphide of carbon; and the fourth scarcely anything but alcohol; a few brown flakes remain in the retort. The decomposition is doubtless at an end when the spontaneous heating ceases; and the heat applied from without serves merely to complete the separation of the two products. The evolution of heat which accompanies the decomposition, seems to show that the alcohol is not contained as alcohol in the xanthic acid. When the acid is distilled with water also, scarcely anything passes over but sulphide of carbon quite free from alcohol, and the residue consists of dilute alcohol, having no acid reaction, together with a few drops of sulphide of carbon. (Zeise.) — According to Couerbe, xanthic acid decomposes spontaneously at all temperatures, with rise of temperature, ebullition, and escape of sulphide of carbon, and leaves a solution of sulphide of carbon in alcohol, or, if water be present, a lower stratum of sulphide of carbon, and an upper one of hydrated alcohol containing sulphide of carbon in solution. — 2. Xanthic acid is easily set on fire, and burns with a bright blue flame, emitting a strong odour of sulphurous acid. (Zeise.) — 3. When exposed to the air, it quickly becomes covered with an opaque crust; the same effect takes

place under water, but more slowly. (Zeise.)—4. Iodine placed in contact with the acid under water, moves about on it in all directions, converts it into a dark red-brown oil, and colours the supernatant water dark brown; on agitation with a somewhat larger quantity of water, colourless aqueous hydriodic acid is obtained, together with a milky oil, which, if a sufficient quantity of iodine has acted on the acid, gives but a dirty yellow turbidity with copper-salts; if the iodine is in excess, the oil remains red-brown. (Zeise.)

Combinations. *Water* takes up but a very small quantity of xanthic acid, acquiring thereby the odour of the acid, but not the power of precipating copper-salts, or even rendering them turbid. (Zeise.)

With Salifiable Bases. Xanthic acid decomposes the alkaline carbonates, with evolution of carbonic acid.—Xanthate of potash or soda is obtained by mixing alcoholic potash or soda with sulphide of carbon; (*vid. Xanthate of potash.*) The other *Xanthates* or *Sulphocarbonates* are obtained, in some cases by direct mixture of the acid with the pure base or its carbonate, in others by precipitating a heavy metallic salt with xanthate of potash. The general formula of the xanthates in the dry state is $C^4H^5MO^2,C^2S^4 = MO,CS^2 + C^4H^5O,CS^2$, and their formation from an acid and a base is attended with the separation of 1 At. water.

$$C^4H^6O^2,C^2S^4 + MO = C^4H^5MO^2,C^2S^4 + HO.$$

All xanthates are decomposed by heat, and when subjected in the dehydrated state to dry distillation, yield principally sulphuretted hydrogen and carbonic acid gases, together with an oily distillate, consisting of *xanthoil*, and leave a mixture of charcoal and metallic sulphide. (Zeise.)

Xanthoil is yellowish, opaque, lighter than water, less volatile than sulphide of carbon, smells strongly aromatic, almost like onions, tastes strongly aromatic and sweetish, and is neutral to vegetable colours. It burns with a bluish flame without smoke, and forms sulphurous acid. It is scarcely soluble in water, does not act on the salts of lead or copper or on cupric oxide, and dissolves readily in alcohol, even when very dilute. (Zeise, *Schw.* 36, 18.)—According to more recent investigations, xanthoil is a mixture of mercaptan [which view, however, appears inconsistent with the above-mentioned behaviour with oxide of copper and its salts], of thialic ether [probably the indifferent oil mentioned on page 349], and probably also a small portion of bisulphide of ethyl. (Zeise, *Pogg.* 25, 506.)

According to Couerbe, xanthates yield by dry distillation a mixture of sulphuretted hydrogen, carbonic acid, and xanthin gases, an oily distillate, consisting of sulphide of carbon, mercaptan, xanthil, and frequently also of xanthurin, and leave a residue consisting of charcoal and metallic sulphide.

Xanthin gas, freed from sulphuretted hydrogen by the solution of a copper salt, smells like mercaptan, but much more disagreeably. It may [according to a very doubtful analysis,] be regarded as $C^2HS^2O^2 = C^2O^2,HS^2$. When set on fire, it burns with a blue flame, forming water, carbonic acid, and sulphurous acid, and depositing sulphur. It is slowly but completely absorbed by strong solution of potash, forming carbonate of potash and transparent crystals of sulphide of hydrogen and potassium. It is likewise completely absorbed by potassium, and forms there-

with a solid mixture of sulphide of potassium, sulphide of hydrogen and potassium, potash, and charcoal, which last remains in the form of a black powder when the other substances are dissolved in water. It is not absorbed by oxide of lead or burnt borax, does not form any black precipitates with metallic salts, or give up its sulphur to melted tin. (Couerbe.)

Xanthil is obtained in the pure state when the oily distillate (xanthoil) is freed from sulphide of carbon, and the greater part of the mercaptan by heating in a retort to 100°; the residue treated with mercuric oxide to remove the remaining portion of mercaptan; the liquid filtered and distilled at a higher temperature in the oil-bath; the xanthil which passes over, freed from accidentally admixed sulphur, sulphide of carbon, and xanthurin, by 24 hours' contact at ordinary temperatures with an equal quantity of alcoholic potash (under which circumstances the sulphur forms sulphide of potassium; the sulphide of carbon, xanthate of potash; and the xanthurin, sulphide of potassium and acetate of potash), and finally by addition of water, which dissolves these three bodies, and causes the xanthil to rise to the surface. Lastly the xanthil is removed, and freed from water by distillation over chloride of calcium. — It is a colourless liquid, of sp. gr. 0·894, which boils at 130°, and has a vapour-density = 3·564; its odour is penetrating and repulsive. It is insoluble in water but dissolves in ether and in alcohol. — Contains 45·650 per cent. C, 9·595 H, 44·752 O, and 0·003 S; hence its formula (disregarding the minute quantity of sulphur) is $C^4H^5O^3$, according to which the vapour must be regarded as monatomic. (Couerbe.)

Xanthurin is principally obtained in the dry distillation of xanthate of lead, towards the latter part of the process, when the heat rises above 140°. The liquid which passes over from 140° upwards must therefore be collected apart; purified by fractional distillation, the portion obtained below 140°, consisting of alcohol, xanthil, &c., being set aside; and finally purified from dissolved sulphur by treatment with strong potash. — Xanthurin is a colourless liquid, of sp. gr. 1·012, vapour-density, 4·542, peculiar but not disagreeable odour, and mild taste. — It contains 46·56 per cent. C, 7·73 H, 15·31 S, and 30·40 O, and has therefore the formula $C^8H^8SO^4$ [this formula does not agree with the experimental vapour-density.] — Xanthurin mixed with alcoholic potash solidifies immediately, alcohol being set free, and a polysulphide of potassium formed together with acetate of potash. (Couerbe.)

These several products distinguished by Couerbe deserve careful examination. Sacc's experiments (p. 455) are unfavourable to Couerbe's statements.

The xanthates are decomposed by nitric acid and by chlorine, the xanthic acid being destroyed; hydrochloric and sulphuric acid separate the xanthic acid in its entire state. — All the alkaline xanthates are soluble in water, and their solutions form with lead-salts a white precipitate, with cupric salts a yellow precipitate, and with mercurous and silver-salts, a precipitate which is yellowish at first, but soon changes to brown and black. (Zeise.)

Xanthate of Ammonia. 1. Obtained by neutralizing the acid with ammonia. — 2. By precipitating an alcoholic solution of xanthate of baryta with an alcoholic solution of sal-ammonic, or an aqueous solution of xanthate of baryta with aqueous sulphate of ammonia, evaporating the filtrate, whereby a certain amount of decomposition takes place, and

freeing the residue from the products of the decomposition just mentioned, by washing with ether, which however, leaves behind but a small portion of salt. (Zeise.) — 3. By the action of ammonia on bioxysulphocarbonate of ethyl, xanthamide being formed at the same time. (Debus, vid. p. 443). — The salt may be partly sublimed without decomposition; the portion which decomposes, yields among other products, a large quantity of sulphocarbonate of ammonium. The salt dissolves very readily in water and alcohol. (Zeise.) — ¶. The aqueous solution of xanthate of ammonia may be evaporated to dryness in vacuo without decomposition. When the solution is left to evaporate freely in the air, a small portion decomposes, with formation of sulphocyanide of ammonium; when evaporated over the water-bath, part of the salt goes off with the aqueous vapour. The crystals are shining, and resembling those of urea.

Dried in vacuo over oil of vitriol.			Debus.
6 C	36	25·90	27·00
9 H	9	6·47	6·83
N	14	10·07	
4 S	64	46·05	
2 O	16	11·51	
$C^4H^5(NH^4)O^2,C^2S^4$	139	100·00	

The great difference between the calculated and analytical results as regards the quantity of carbon arises from the instability of the salt. As a verification of the formula, Debus prepared the lead-salt by precipitating the ammonia-salt with acetate of lead, and obtained a salt whose composition agreed closely with the calculated quantities (vid. p. 458).

Xanthate of ammonia heated in a test-tube gives off a white sublimate, sulphide of ammonium, a yellow oily body, probably also sulphocarbonate of ammonium, and leaves a small black residue. When kept either in solution or in the dry state, it decomposes with evolution of ammonia. The salt does not appear to be altered by boiling for a short time with ammonia; but if left for several days in contact with that substance, it yields small quantities of sulphide and sulphocyanide of ammonium.— Sulphide of ammonium boiled with the salt or left in contact with it for some time, decomposes it, with formation of products which do not contain sulphocyanide of ammonium, but have not yet been further examined. (Debus, *Ann. Pharm.* 72, 9.) ¶.

Xanthate of Potash. — Formed by mixing alcoholic potash with sulphide of carbon, or an alcoholic solution of sulphide of carbon with hydrate of potash; if the air be excluded, xanthate of potash is the only product obtained by this action. 47·2 pts. (1 At.) of dry potash require to neutralize them, besides alcohol, 75·7 pts. (76 pts. = 2 At.) sulphide of carbon, and yield 162 pts. (160·2 pts. = 1 At.) of dry xanthate of potash. (Zeise.) This salt is also formed by the action of carbonate of potash on alcoholic sulphide of carbon, but slowly and with simultaneous production of bicarbonate of potash. (Zeise.) — The alcoholic potash is never completely neutralized, even when the sulphide of carbon is in excess; and the mother-liquor separated from the crystallized xanthate of potash, yields on evaporation, not only xanthate of potash, but also hyposulphite of potash, polysulphide of potassium, and charcoal mixed with sulphur. (Couerbe.) [Are these conflicting results due to the presence of water in the alcohol or to access of air?].

Preparation. 1. Finely pulverized hydrate of potash is added in successive portions and with agitation to a solution of 1 pt. sulphide of carbon in 18 pts. absolute alcohol, till only a small portion of sulphide of carbon remains in excess, and consequently a sample of the liquid mixed with 8 times its bulk of water gives but a slight turbidity and does not redden turmeric paper. The liquid is left to subside for a short time, then decanted and filtered quickly through paper, without bringing the deposit on the filter, because it may still contain hydrate potash. — *a.* The resulting filtrate placed in a wide-mouthed bottle and surrounded with ice, changes in a few hours to a crystalline mass of salt. This product is thrown on a calico filter; the mother-liquid, which is generally somewhat yellowish, allowed to run off; the crystals repeatedly washed with small quantities of ice-cold absolute alcohol, till the liquid which runs through no longer forms a cloud with water; and then immediately introduced into a wide-mouthed and well stoppered glass bottle. — *b.* The deposit containing hydrate and xanthate of potash, is immediately mixed with a little absolute alcohol, and — if a sample of the mixture diluted with water reddens turmeric — also with a small additional quantity of sulphide of carbon. The yellowish mother-liquor of *a* is then likewise added, the bottle heated to 60° in warm water, and agitated; the liquid filtered; and the xanthate of potash left to crystallize from the filtrate as in *a*. A few more crystals may still be obtained by treating the deposit which remains on the filter with the mother-liquor obtained in this last process. (Zeise.)

2. Absolute alcohol is saturated at 18° — 20° with hydrate of potash, by setting the mixture aside and shaking it up now and then; the filtered [or decanted] liquid shaken up immediately before it begins to turn brown, with about $\frac{1}{32}$ of its volume of sulphide of carbon; after which the addition of sulphide of carbon is continued by small portions of $\frac{1}{32}$ of the volume, till the liquid just loses its alkaline reaction, and a sample of it becomes milky when mixed with water, showing that a slight excess of sulphide of carbon is present. The mixture is then cooled to 0° for three quarters of an hour; the solidified mass thrown on a filter (addition of ether makes the salt crystallize better and accelerates its descication); pressed several times between paper; and lastly dried in vacuo over oil of vitriol and preserved in air-tight vessels. — Evaporation, even in vacuo, does not yield so pure a salt. (Zeise.)

3. A solution of 3 pts. hydrate of potash in 4 pts. absolute alcohol is shaken up in a bottle with 4 pts. sulphide of carbon; the liquid poured into a basin as soon as it begins to deposit crystals; and after six hours, the resulting crystals placed upon linen, washed with ether, and pressed at the same time. (Couerbe.)

4. Alcohol saturated with pure hydrate of potash and shaken up with excess of sulphide of carbon, solidifies immediately in a crystalline mass, which must be quickly washed on a filter with ether, pressed between blotting paper, and dried under a bell-jar over oil of vitriol. — If very highly rectified spirit be used, the salt crystallizes out when cooled to a low temperature, or on addition of ether; hence the solution must be evaporated under 50°. (Sacc, *Ann. Pharm.* 51, 345.)

Properties. Colourless (or yellowish white) needles having a silky lustre; neutral, of faint peculiar odour, and strong, cooling, sulphurous

taste. The solution of the salt colours the skin yellow. (Zeise.) The salt has an alkaline reaction, and an intolerably bitter taste, like that of aloes. (Couerbe.)

	Crystallized.			Zeise.	Couerbe.
KO	47·2	....	29·46	29·37	29·89
6 C	36·0	....	22·47	22·69	22·25
5 H	5·0	....	3·12	3·19	3·04
O	8·0	....	5·00	4·85	4·26
4 S	64·0	....	39·95	39·90	40·56
C^4H^5KO,C^2S^5	160·2	....	100·00	100·00	100·00

The crystals examined by Zeise had been previously dried in vacuo.

Decompositions. 1. The salt, when subjected to dry distillation, begins to decompose at 200°, and gives off, with fusion and ebullition, carbonic acid, sulphuretted hydrogen, and xanthoil (p. 450), leaving a light red mass, which, when exposed to the air, gradually becomes moist and yellow. This light red mass forms with water a clear, strongly alkaline, red liquid, which turns brown in a few minutes, and when mixed with hydrochloric acid, effervesces violently, emitting an odour of sulphuretted hydrogen and sulphide of carbon, and yielding a small quantity of oily matter. This red liquid forms no precipitates with baryta-salts; with lead-salts, a light red precipitate, soon turning black; with copper-salts, black-brown; with corrosive sublimate, a yellow precipitate turning greyish white in a few hours; and with cyanide of mercury, a yellowish brown colouring, and after a few hours, a black-brown precipitate. Alcohol dissolves only a portion of the light red mass, while a whitish saline substance remains. — The light red mass, when more strongly heated in the retort, gives off with intumescence, an additional quantity of xanthoil, together with a small quantity of gas; fuses quietly at a temperature below redness; and separates on cooling into an upper brown amorphous stratum and a lower grey metallic stratum. — The lower stratum deliquesces quickly in the air and dissolves completely in water, forming a black-brown alkaline liquid, which, when treated with acids, gives off sulphuretted hydrogen and deposits a small quantity of sulphur. — When the two strata of liquid are still more strongly heated, a small additional quantity of gas is evolved, but no more oil; as the temperature approaches redness, a slight incandescence is produced; and there remains a black mixture of charcoal and persulphide or potassium. (Zeise.) — 100 pts. of xanthate of potash are resolved by dry distillation in the oil-bath at 200°, into 13·05 pts. of a gaseous mixture consisting of carbonic acid, carbonic oxide, xanthin (p. 450), and a trace of sulphuretted hydrogen; — 29·20 parts of an oil consisting of a large quantity of mercaptan mixed with xanthil (p. 451), free sulphur in a state of solution, a trace of sulphide of carbon, and sometimes also with xanthurin; — and 54·95 pts. of a crude residue consisting of charcoal and persulphide of potassium (also containing hyposulphite of potash formed in consequence of access of air), which, however, dissolves completely in water, and on addition of an acid deposits 7·5 pts. of charcoal mixed with sulphur in light flakes. (Couerbe.) — The perfectly dry salt, heated to 280° over a charcoal fire, assumes an orange-yellow colour, the change proceeding from without inwards; then blackens; then, as the heat increases, evolves carbonic oxide and sulphuretted hydrogen; yields a distillate consisting of pure mercaptan

together with a small quantity of water; and leaves a residue of bisulphide of potassium mixed with shining spangles of charcoal:

$$2(C^4H^5KO^2,2CS^2) = 2HS + 2CO + 2HO + C^4H^6S^2 + 2KS^2 + 6C.$$

If the salt be heated merely to 200° in the oil-bath, the same products are obtained, but the mercaptan contains traces of sulphide of carbon, and the decomposition is incomplete. But the new products mentioned by Couerbe are not obtained. (Sacc.) — Xanthate of potash subjected to dry distillation, in contact with sulphur yields a heavy oil, which smells exactly like bisulphide of ethyl. (Zeise.)

2. The concentrated aqueous solution of the salt, when subjected to distillation, immediately becomes alkaline, and after a time yellowish brown and gives off nothing but alcohol, sulphide of carbon, and sulphuretted hydrogen; if the distillation be carried on continuously, with frequent renewal of the water, till nothing but a small quantity of sulphuretted hydrogen passes over, a red-brown residue is left consisting of sulphide of potassium, sulphocarbonate of potassium, carbonate of potash, and hyposulphite of potash. (Zeise.) — When a quantity of water, not sufficient to dissolve the salt in the cold, is gradually heated with it over a charcoal fire, the liquid becomes brownish yellow in the lower part at 30°, and throughout at 80° (from formation of sulphocarbonate of potassium), then darker at 100°, with evolution of carbonic acid and sulphuretted hydrogen, and yields a distillate consisting of alcohol, sulphide of carbon, and a very small quantity of mercaptan, while aqueous sulphide of potassium remains behind. (Sacc.) Probably as represented by the equation:

$$C^4H^5KO^2,2CS^2 + 2HO = CO^2 + HS + CS^2 + C^4H^6O^2 + KS.$$

(Sacc.) [The passage in *Ann. Pharm.* 51, 347, is obscure.] — When a solution of the salt in hydrated alcohol is distilled below 100°, the same products are obtained, excepting that no sulphide of carbon passes over, that compound in fact remaining in the dark orange-yellow residue in combination with sulphide of potassium. (Sacc.) — When a concentrated aqueous solution of xanthate of potash is distilled with hydrate of potash, alcohol passes over together with a large quantity of mercaptan. (Zeise.)

3. The crystals, when exposed to the air, assume a yellowish colour, and their aqueous solution becomes milky under the same circumstances. (Zeise.) — 4. Chlorine, even at ordinary temperatures, decomposes xanthate of potash with evolution of heat, forming chloride of potassium, a combustible sulphurous gas, and an oil which has a powerful odour, like that of hydrochloric acid, reddens litmus strongly, and burns with a greenish flame. (Zeise.) — 5. Iodine triturated with xanthate of potash and a small quantity of alcohol forms xanthic ether. (Zeise, *vid.* p. 439.) — Iodine at ordinary temperatures merely abstracts the potassium and separates the compound $C^4H^5O^1,C^2S^4$, which afterwards yields xanthic ether when heated. (Desains, Debus, *vid.* p. 439.) — 6. Fuming nitric acid decomposes the salt so violently that individual particles of it are often set on fire; when it acts in excess, it converts the sulphur of the salt into sulphuric acid. (Zeise.) — 7. Fluosilicic acid gas yields silicofluoride of potassium and a number of complicated products. — Hydrochloric acid gas acts violently, evolving sulphide of carbon and a peculiar ethereal substance. Sulphurous acid gas converts the dry salt into hyposulphite of potash, with evolution of mercaptan and other substances.

Aqueous phosphoric, sulphuric, or hydrochloric acid separates oily xanthic acid without any effervescence. (Zeise.)

Xanthate of potash does not become moist on exposure to the air (unless it contains sulphide of potassium: *Couerbe*), but dissolves quickly and abundantly in water, forming a solution which is yellowish only when concentrated. (Zeise.) — It dissolves in 5 or 6 parts of absolute alcohol; the solution, when evaporated, has a strong tendency to form efflorescences. It may be boiled down in a retort without decomposition; but if the alcohol contains water, even so little as 8 per cent., the same decomposition takes place as in the aqueous solution. — Ether dissolves the salt very sparingly, and precipitates it from its alcoholic solution in needles. Rock-oil does not dissolve it at all. (Zeise.)

Xanthate of Soda. — Prepared like the potassium-salt (method 2). The neutralization of the alcoholic soda by the sulphide of carbon takes place somewhat more slowly than that of the potash. The alcoholic solution evaporated over chloride of calcium in slightly rarefied air, leaves sometimes a colourless, sometimes a yellow mass made up of needles. (Zeise.) The dry salt contains 21·54 p. c. of soda. (Zeise.)

Xanthate of Baryta. — A solution of sulphide of carbon in absolute alcohol is briskly agitated for several hours with a quantity of finely pulverized anhydrous baryta or fused hydrate of baryta, just sufficient to leave the sulphide of carbon a little in excess, and the filtrate quickly evaporated in vacuo over chloride of calcium, and then over oil of vitriol.

If anhydrous baryta has been used, the liquid evaporated in vacuo over chloride of calcium, leaves a pasty mass, which, if then left in as perfect a vacuum as possible over oil of vitriol, gives off gas-bubbles, and is converted into a hard body, yielding a white powder, and containing 40·402 p. c. baryta, therefore $= C^4H^5BaO^2,C^2S^4$. But, on the addition of a small quantity of water, the pasty mass obtained by drying over chloride of calcium, which perhaps contains 1 At. water, quickly passes into the solid, crystalline state; and its solution in a larger quantity of water, when left to evaporate in vacuo, forms transparent and colourless leaves and stars, which appear to contain 2 At. water. — The baryta-salt is very prone to decomposition, which takes place even during the drying of the crystallized salt, also when it is kept in close vessels, and during the evaporation of the aqueous and even of the alcoholic solution in rarefied air at ordinary temperatures; this spontaneous decomposition is attended with the formation of hyposulphite of baryta. When the aqueous or alcoholic solution is gently heated, complete decomposition takes place, attended with the formation of the same products as in the decomposition of the potash-salt. By dry distillation, a distillate is obtained containing mercaptan. (Zeise.)

Xanthate of Lime. — Formed in a similar manner by shaking up hydrate of lime with an alcoholic solution of sulphide of carbon; but the action is very slow, and on evaporating the filtrate, the salt remains in the form of a gum. (Zeise.)

Aqueous xanthate of potash does not precipitate hydrochlorate of *Magnesia* or *Alum*. (Zeise.)

Aqueous xanthate of potash forms a yellowish precipitate with hydrochlorate of *Antimonic oxide* and nitrate of *Bismuth*. (Zeise.)

Xanthate of Zinc. — Xanthate of potash added to sulphate of zinc throws down white, heavy, crystalline, granules which become greenish white on exposure to the air. The salt melts when strongly heated in contact with the air, throwing off bubbles and forming a light green mass, which, when treated with hydrochloric acid, gives off a gas having an odour like that of sulphuretted hydrogen, but at the same time peculiar to itself; solidifies at a higher temperature; but as the heat rises still higher, again becomes liquid, assuming a blackish tint, and here and there a metallic appearance; and ultimately disappears almost entirely. — The salt dissolves sparingly in water, more readily in alcohol, even when weak; the alcoholic solution yields, on evaporation, a white, tolerably hard, amorphous mass. (Zeise.)

Stannous Xanthate. — Xanthate of potash forms a yellowish precipitate with protochloride of tin.

Xanthate of Lead. — Formed by bringing oxide of lead in contact with xanthic acid, or as a white precipitate, on mixing nitrate or acetate of lead with the acid or its potash-salt. — 1. An aqueous solution of xanthate of potash is first precipitated by a slight excess of nitrate of lead, and afterwards xanthate of potash added in slight excess. If the potash-salt is in excess from the beginning, the precipitate runs through the filter. — 2. An alcoholic solution of acetate of lead is precipitated by an alcoholic solution of xanthate of potash. In this case, a crystalline precipitate is formed, but not till after some time; it may be dried in the air without decomposition. (Zeise.) — 3. A very dilute aqueous solution of acetate of lead is precipitated by aqueous xanthate of potash, the precipitate washed with hot water, then with alcohol, and dried by heat or by exposure to the sun. (Couerbe.) When heavy metallic salts are precipitated by xanthate of potash in aqueous solutions of too great a degree of concentration, part of the xanthic acid is decomposed, and xanthurin containing sulphur is produced in the form of a yellow, strongly smelling oil. As soon as this substance makes its appearance, the liquid must be strongly agitated to reproduce the compound; but the precipitate thereby obtained is less pure in colour, odorous, and greasy to the touch. (Couerbe.) — 4. To obtain the salt in crystals, the precipitate must be dissolved in alcohol at 40°—45°, and the solution cooled to the crystallizing point. Boiling would decompose the salt and form sulphide of lead, which would contaminate the crystals. It is necessary therefore to use a considerable quantity of alcohol, inasmuch as that liquid does not dissolve much more of the salt at 45° than at ordinary temperatures. (Couerbe. — ¶ 5. An alcoholic solution of potash mixed with quantities of sulphide of carbon and hydrated oxide of lead equivalent to the potash, then set aside for 6 or 8 hours, and frequently shaken, deposits a mixture of sulphide of lead and large colourless crystals of xanthate of lead; another portion of the latter remains in solution, and, on addition of water, separates from the filtrate in long colourless needles. (Debus, *Ann. Pharm.* 72, 2.) ¶

The dried precipitate (1) is a greyish white, somewhat nacreous, soft, light, nearly inodorous powder. (Zeise.) The precipitate (3) is a pale yellowish white, amorphous powder, which turns black even when kept in a stoppered bottle. (Couerbe.) The salt crystallized by (2) assumes the forms of colourless needles and of crystalline wool (Zeise); that which is obtained by (4) crystallizes in long soft, yellowish, needles which have a silky lustre and do not blacken by keeping. (Couerbe.)

				Zeise.	Lieb. & Pelouze. (*A. Pharm.* 19, 260).	Couerbe. *Crystallized.*	Debus. *Crystallized.*
PbO	112	49·78		49·64	49·58		49·30
6 C	36	16·00		16·18	16·20	15·69	16·11
5 H	5	2·22		2·20	2·21	2·26	2·41
O	8	3·55					
4 S	64	28·45					29·15
$C^4H^5PbO^2,C^2S^4$	225	100·00					

The salt is permanent in the air, acquires a peculiar odour by long keeping, and sustains a gentle heat without decomposition. When subjected to dry distillation, it blackens, then fuses, boils up, and gives off a small quantity of a gaseous mixture having an alliaceous odour and consisting mainly of sulphuretted hydrogen and carbonic acid, and yields a distillate of xanthoil; the residue then solidifies, exhibits a glimmering light before the heat rises to redness, and is then composed of charcoal and sulphide of lead. (Zeise.) — The decomposition of the salt begins at 60° and is complete at 200°. The gaseous mixture thereby evolved amounts to 8·72 per cent. of the lead-salt, and consists of xanthin-gas with small quantities of sulphuretted hydrogen and carbonic acid. The total quantity of the distillate is 33·94 p. c., and the residue, which has a peculiar odour, amounts to 57·34 p. c.; and consists of sulphide of lead with small quantities of excess of sulphur and charcoal (amounting to 2 p. c. of the xanthate of lead). — The first distillate is colourless, the last yellowish. — The portion obtained between 60° and 100° consists almost wholly sulphide of carbon with a little mercaptan; between 100° and 120°, a large quantity of alcohol passes over, together with small quantities of mercaptan and xanthurin, and traces of sulphide of carbon and xanthil; at a stronger heat, the product consists almost wholly of xanthurin. (Couerbe.) — Decomposition begins at 122°; at 140°, a yellow oil of variable boiling point distils over, without evolution of gas, while sulphide of lead amounting to half the weight of the original salt remains behind. (Debus.) — Nitric acid of 40° Bm. quickly dissolves xanthate of lead without evolution of gas, leaving a yellowish buttery mass. (Zeise.) Dilute nitric acid converts it in a few hours into a fatty substance; by longer contact with the dilute acid, or by the action of strong nitric acid, it is converted into a yellow oil and sulphate of lead. — Oil of vitriol separates the xanthic acid with tolerable quickness, but if even slightly diluted with water, it acts very slowly. — Dry hydrochloric acid gas acts upon the lead-salt in the same manner as on the potash-salt; aqueous hydrochloric acid quickly separates the xanthic acid in oily drops. (Zeise.) Sulphuretted hydrogen gas does not act on the dry lead-salt, even after a long time (Zeise, Debus); the aqueous or alcoholic solution of the gas blackens the salt very slowly, and without separating any appreciable quantity of xanthic acid; but aqueous hydrosulphate of ammonia, potash, or baryta decomposes the salt immediately, forming sulphide of lead and xanthate of the alkali. (Zeise.) — Xanthate of lead heated with a dilute aqueous or alcoholic solution of potash or ammonia gradually blackens, while a xanthate of the alkali is formed in the liquid; an excess of strong potash-ley first dissolves the entire salt, and afterwards, when more strongly heated, deposits a black mixture of sulphide, oxide, or carbonate of lead. (Zeise.) — Xanthate of lead is very slowly blackened by boiling with pure water (Zeise), with separation of sulphide of lead, sulphide of ethyl, and pro-

bably also of hyposulphurous acid. (Debus.) — When immersed in the aqueous solution of a cupric salt, it quickly forms cuprous xanthate. (Zeise.) — Iodine decomposes xanthate of lead, forming iodide of lead and bioxysulphocarbonate of ethyl. (Debus, p. 441.)—Xanthate of lead is insoluble in water and in ether; it is likewise nearly insoluble in cold alcohol, but dissolves with tolerable facility in hot alcohol. (Zeise, Couerbe.)

Cuprous Xanthate. — Formed by the action of xanthic acid on cupric oxide, or of an alkaline xanthate on a cupric salt. In the latter case, a black precipitate [of cupric xanthate?] is produced, which, in a few seconds, changes to the beautiful yellow and flocculent precipitate — or curdy if the solutions are concentrated — of cuprous xanthate. As a cupric salt is hereby converted into a cuprous salt, the xanthic acid likewise undergoes partial decomposition, the chief product of which is *Xanthelene*, a large quantity of free sulphur being likewise separated. (Zeise.)

To obtain the *Xanthelene* in a state of purity, an alcoholic solution of cupric chloride is precipitated by an alcoholic solution of xanthate of potash; the liquid separated by filtration from the cuprous xanthate; the greater part of the alcohol distilled off from the filtrate; the residue mixed with ether; and the mixture filtered from the separated sulphur and chloride of potassium, then shaken up with water, and left at rest, whereupon a lower stratum of liquid is formed containing water and alcohol, and above it a solution of xanthelene in ether. The ether is next distilled off; the residue evaporated in vacuo over oil of vitriol; and the xanthelene, which remains behind and still contains free sulphur in solution, is distilled after the addition of solution of common salt; it then passes over undecomposed, though very slowly, together with the aqueous vapours. Finally, the distillate is dehydrated by contact with chloride of calcium.

Xanthelene is a pale yellow oil of sp. gr. 1·105 and peculiar odour.

It contains 39·0 p. c. C and 6·6 H, and is perhaps isomeric with xanthic ether, C^4H^5O,CS^2. It cannot be distilled without decomposition, except in presence of water; when distilled alone, it becomes charred and yields a distillate having an odour very much like that of xanthoil obtained from xanthate of potash. The solution of xanthelene in alcoholic potash appears to be accompanied by the formation of xanthate of potash and sulphide of potassium. Iodine dissolves in xanthelene, imparting a brown colour to it and apparently without decomposing it. (Zeise.)

With this is connected the statement of Couerbe (*Ann. Chim. Phys.* 6, 247), that ether extracts from the xanthate of copper obtained by precipitating a cupric salt with xanthate of potash, a greenish oil crystallizing in beautiful prisms, which melt even when placed on the hand, and, like olefiant gas, appear to contain C and H in equal numbers of atoms. [These easily fusible crystals have likewise some resemblance to bioxysulphocarbonate of ethyl.]

¶. Debus is of opinion that the oxidized product obtained by the action of protochloride of copper on xanthate of potash is isomeric with bioxysulphocarbonate of ethyl, and that the xanthic ether obtained from that compound at higher temperatures is isomeric with Zeise's *Xanthelene;* for if, after treating the alcoholic solution of xanthate of potash with protochloride of copper, the liquid be filtered from the cuprous xanthate, and the filtrate diluted with water, an oily body is precipitated, which,

when dissolved in alcohol, cannot be crystallized even by cooling to 0°, but in other respects agrees pretty well with bioxysulphocarbonate of ethyl, and when distilled at a high temperature, yields a substance apparently identical with xanthelene. The decomposition of xanthate of potash by protochloride of copper appears to take place in the manner represented by the following equation:

$$2(C^4H^5KO^2,C^2S^4) + 2CuCl = 2KCl + C^4H^5Cu^2O^2,C^2S^4 + C^4H^5O^2,C^2S^4.$$

(Debus, *Ann. Pharm.* 72, 7.) In a later communication, however, *Ann. Pharm.* 75, 146) Debus states that the salt hitherto regarded as cuprous xanthate is really a compound of cupric xanthate with cuprous sulphide: $3(C^4H^5CuO^2,C^2S^4)+Cu^2S$; in fact that the action of xanthate of potash on cupric salts is precisely analogous to that of oxyxanthate of potassium on cupric sulphate (*vid.* p. 464). ¶

To prepare cuprous xanthate, an alcoholic solution of cupric chloride or acetate is precipitated by an excess of alcoholic xanthate of potash, and the precipitate washed, first with alcohol, till the liquid which runs through no longer becomes turbid (from separation of xanthelene) on addition of water, then with water, and dried in the air, by which it does not suffer decomposition. (Zeise.) — The alcoholic filtrate, when set aside for a few weeks, deposits peculiar crystals. — If the compound be precipitated from aqueous solutions, xanthelene and sulphur remain mixed with the cuprous xanthate, and impart to it a peculiar herb-like odour, from which it can only be purified by continued washing with alcohol, or better with ether. (Zeise.)

			Zeise.
Cu^2O	72	38·92	38
6 C	36	19·46	
5 H	5	2·70	
O	8	4·32	
4 S	64	34·60	
$C^4H^5Cu^2O^2,C^2S^4$	185	100·00	

Cuprous xanthate when distilled, first gives off an oily liquid without changing its colour, then blackens, yields more oil, and, both before and during ignition, a gas having a peculiar odour. Nitric acid of 35° Bm. forms with the salt a greenish solution, the formation of which is attended with brisk effervescence, and separation of an opaque, fatty, blackish mass, soon changing however to yellowish white. — Cold oil of vitriol acts very slowly on the salt; on the application of a gentle heat, it forms a greenish mixture (from which the yellow salt is again separated by water) and on the continued application of a stronger heat, produces complete decomposition. — Strong hydrochloric acid acts very slowly in the cold, and does not destroy the yellow colour of the salt; but when heated, it separates xanthic acid and forms a solution of cuprous chloride in hydrochloric acid. Sulphuretted hydrogen water does not act much upon the salt, but aqueous sulphide of potassium blackens it instantly. — Ammonia dissolves but very little of the salt at ordinary temperatures; when heated, it dissolves rather more, forming a greenish blue solution; the undissolved portion presents the original characters of the salt, excepting that a few granules appear blackish. Aqueous potash at 100° changes the yellow colour of the salt to black-brown. — The salt, at the moment of precipitation from alcoholic mixtures, appears to be

slightly soluble in excess of xanthate of potash, and of cupric acetate. (Zeise.)

Mercurous Xanthate. — A concentrated aqueous solution of xanthate of potash forms a black precipitate with mercurous nitrate; a more dilute solution forms a yellow precipitate, which however, in a few minutes, especially under the influence of light, becomes first brown and afterwards black.

Mercuric Xanthate. — Xanthate of potash forms with aqueous hydrochlorate or hydrocyanate of mercuric oxide, a white precipitate, which is at first very finely divided and runs through the filter, but afterwards becomes sandy; it is soluble in excess of xanthate of potash. It becomes yellowish in a few months. When heated, it turns yellow and then black; melts somewhat above 100°; gives off, with intumescence, a small quantity of gas having an alliaceous odour, and a large quantity of xanthoil; afterwards yields a dark grey sublimate, red when pulverized [cinnabar?], and leaves a black residue of charcoal.

Xanthate of Silver. — Concentrated solutions of xanthate of potash and nitrate of silver form a black precipitate, more dilute solutions a yellowish precipitate which, especially under the influence of light, turns brown in a few minutes and afterwards black. (Zeise.) The precipitate contains 50·57 p. c. of oxide of silver. (Liebig & Pelouze, *Ann. Pharm.* 19, 260.)

¶ Oxyxanthic Acid. $C^4H^6S^2,2CO^2$?

DEBUS. *Ann. Pharm.* 75, 128; Jahresber. 1850, 464.

This acid has not been obtained in the free state. The action of strong sulphuric acid on its potassium-salt appears to isolate it; but the experiments hitherto made on this point are not decisive (*vid.* p. 462) The potassium salt is formed by the action of alcoholic potash on xanthic ether; and from the solution of this compound, the lead and silver salts, and one or two others are obtained by double decomposition. The term *Oxyxanthates* applied to this class of salts denotes that they may be regarded as derived from the xanthates by the substitution of 2 At. O for 2 At. S; e. g., *Xanthate of potash* = $C^4H^5O^2,2CS^2 = C^6H^5S^4O^2$; *Oxyxanthate* = $C^4H^5S^2,2CO^2 = C^6H^5S^2O^4$. Debus regards them as carbonates of ethylo-metallic sulphides; e. g., the potassium-salt, as *bicarbonate of ethylo-potassic sulphide* (*Kohlensaures Aethyl-Kaliumsulfuret*) = $C^4H^5S,KS,2CO^2$, &c.

Oxyxanthate of Potassium. — When a solution of xanthic ether in the smallest possible quantity of 90 per cent. alcohol is mixed with twice its weight of potash in the state of concentrated alcoholic solution, the mixture left to stand for some time in a cold place, and ultimately cooled down to 0°, this salt is deposited in crystals, leaving a mother-liquor containing mercaptan (*vid.* p. 441).

$$2(C^4H^5O,CS^2) + KO,HO = C^4H^5KS^2,2CO^2 + C^4H^6S^2.$$

Crystallizes from strong solutions quickly cooled, in long thin needles; but by slow crystallization, it is obtained in colourless, shining, prismatic

crystals, which appear to be isomorphous with those of xanthate of potash. (Debus.)

			Debus.
6 C	36·0	24·94	
5 H	5·0	3·46	
K	39·2	27·23	27·15
2 S	32·0	22·18	21·96
4 O	32·0	22·19	
$C^4H^5KS^2,2CO^2$	144·2	100·00	

1. *Decompositions.*—This compound when heated in a tube, decomposes, turning black and giving off a vapour which smells like xanthic ether and condenses to a colourless liquid. The residue, if heated to redness, gives off small quantities of a pungent vapour, but is not otherwise perceptibly altered; on cooling it solidifies in a black mass which dissolves in water, forming a sepia-coloured solution, and in the moist state blackens silver strongly.

2. This compound, when perfectly dry, may be preserved without alteration; but when enclosed in the moist state in a well-stoppered bottle, it decomposes after a while, yielding sulphuretted hydrogen, bicarbonate of potash, and alcohol.

[Probably thus: $C^4H^5KS^2,2CO^2 + 3HO = C^4H^6O^2 + 2HS + KO,2CO^2$.]

The same products are obtained on boiling the compound with alcohol.—3. The aqueous solution decomposes spontaneously in a few days at ordinary temperatures, and instantly at a boiling heat, into carbonate of potash, sulphide of potassium, mercaptan and alcohol.—This decomposition cannot be expressed by an equation.]—4. Aqueous acids decompose the compound, forming alcohol, carbonic acid, sulphuretted hydrogen, and a potash-salt of the acid: *e.g.*

$$C^4H^5KS^2,2CO^2 + SO^3,HO + 2HO = C^4H^6O^2 + 2HS + 2CO^2 + KO,SO^3.$$

Strong sulphuric acid dissolves the compound without evolution of gas; but on adding a few drops of water, carbonic acid and sulphuretted hydrogen are rapidly evolved.

[This experiment seemed to show that the compound $C^4H^6S^2,2CO^2$ (analogous to xanthic acid, $C^4H^6O^2,2CS^2$) might be separated from the potassium-salt by the action of strong acids. Debus therefore endeavoured to isolate it by the action of dry hydrochloric acid gas; but the products were the same as with the aqueous acid; neither was the acid obtained by introducing the dry potassium-compound into hydrochloric acid.]

5. The aqueous solution boiled with potash and hydrated oxide of lead, yields sulphide of lead, carbonate of potash, and alcohol:

$$C^4H^5KS^2,2CO^2 + 2(HO,PbO) + KO = 2PbS + 2(KO,CO^2) + C^4H^6O^2 + HO.$$

[In these several reactions, the alcohol was never directly recognized among the other products. As, however, no other body was found among them, and the occurrence of alcohol agrees with the equations, Debus considers that its presence may be relied on with tolerable certainty. It must be observed, however, that some of the reactions are not very clearly made out].

6. Iodine abstracts the potassium and leaves bicarbonate of bisulphethyl, $C^4H^5S^2,2CO^2$.

7. A solution of oxyxanthate of potassium is not precipitated by the soluble salts of the alkalis or alkaline earths, or by the sulphates of cadmium, nickel, zinc, or chromium. Acetate of lead produces a white crystalline precipitate of oxyxanthate of lead; and nitrate of silver, a

white curdy precipitate of oxyxanthate of silver. — Sulphate of copper forms a yellowish precipitate impregnated with an oily substance. Corrosive sublimate forms a scanty white precipitate, probably containing subchloride of mercury, while a yellow oily body rises to the surface of the liquid. — 8. With chloride of ethyl it forms chloride of potassium and carbonate of sulphethyl (*vid.* p. 445).

Combinations. — This salt dissolves very readily in water, but is not deliquescent. It dissolves very easily in alcohol at 15° — 20°, sparingly at 0°. Ether dissolves but very little of it, and when added to the alcoholic solution, throws down the greater part of the salt in small crystals. (Debus.)

Oxyxanthate of Zinc. — A concentrated aqueous solution of the potassium-salt mixed with a saturated solution of sulphate of zinc, produces no precipitate; and on evaporating the liquid in vacuo, part of the oxyxanthate of zinc produced by the mixture is decomposed, with evolution of carbonic acid and separation of sulphide of zinc. The dry mass is treated with a small quantity of absolute alcohol to separate sulphate of potash and sulphide of zinc, and dissolve the undecomposed portion of oxyxanthate of zinc. When the solution is evaporated in vacuo, a small portion of the salt is again decomposed, but the greater part remains unaltered, being merely contaminated with a small quantity of sulphide of zinc. — White tallowy mass, which dissolves with tolerable facility in water and alcohol. — When the solutions are left to themselves at ordinary temperatures, or when they are gently heated, decomposition takes place, carbonic acid and sulphide of zinc being separated. The other transformations of this salt are for the most part analogous to those of the potassium-salt. (Debus.)

Oxyxanthate of Lead. $C^4H^5PbS^2,2CO^2$. — Precipitated in the form of a white crystalline powder when acetate of lead is added to a solution of oxyxanthate of potassium in equivalent quantity. An excess of either of the two salts would redissolve the precipitate. On evaporating the solution, the salt is obtained in white, shining needles arranged in concentric groups, and exhibiting under the microscope the form of prismatic crystals, with two of their opposite lateral faces very much developed. The best crystals are obtained by dissolving the salt in alcohol of 50°, and leaving the solution to evaporate slowly in the air. — This salt heated in a test-tube is resolved at about 100° into sulphide of lead, and an ethereal substance which condenses on the colder parts of the tube. When boiled with water, it also yields sulphide of lead and a substance having a peculiar and offensive odour. — Acetic acid has no action upon the salt; but sulphuric, hydrochloric and nitric acid decompose it, with evolution of sulphuretted hydrogen and carbonic acid. — Iodine decomposes it like the potassium salt. — Sulphuretted hydrogen passed through water in which the salt is suspended, throws down sulphide of lead and forms other products not yet examined. Sulphide of ammonium acts in a similar manner. Sulphide of potassium forms sulphide of lead and oxyxanthate of potassium. — Aqueous ammonia has no action on the salt. — Caustic potash dissolves it at ordinary temperatures; forming a clear solution, which after long standing, or instantly at ordinary temperatures, deposits sulphide of lead. — The salt is insoluble in water, but dissolves sparingly in alcohol and ether. (Debus.)

				Debus.
6 C	36	17·24		17·18
5 H	5	2·39		2·36
Pb	104	49·71		49·43
2 S	32	15·33		
4 O	32	15·33		
$C^4H^5PbS^2,2CO^2$	209	100·00		

Oxyxanthate of Copper. — A concentrated solution of oxyxanthate of potassium added to a solution of sulphate of copper, forms a precipitate of oxyxanthate of copper, which is white at the first moment of its formation but quickly becomes yellowish and changes into an unctuous mass which adheres closely to the glass. This mass is a mixture of two new bodies $3(C^4H^5CuS^2,2CO^2)+Cu^2S$ and $C^{12}H^{10}S^3O^8$, (p. 448), resulting from the decomposition of the oxyxanthate of copper:

$$5(C^4H^5CuS^2,2CO^2) = [3(C^4H^5CuS^2,2CO^2) + Cu^2S] + C^{12}H^{10}S^3O^8.$$

These bodies may be separated by washing the mass on a filter with water, then dissolving in cold alcohol, filtering again, and evaporating the solution in vacuo. The dry residue, after repeated washing with ether and finally with water, leaves the compound $3(C^4H^5CuS^2,2CO^2)+Cu^2S$, which may be dried in vacuo; and the ethereal extract evaporated in the air at ordinary temperatures leaves the compound $C^{12}H^{10}S^3O^8$ in the form of an oil having a faint yellowish tint. (Debus.)

Oxyxanthate of Copper with Disulphide of Copper. — This is the first of the above-mentioned products of the decomposition of oxyxanthate of copper. — Yellow, non-crystalline powder; when heated in a test-tube, it is resolved below 100° into a tarry mass which, at a higher temperature, gives off an ethereal liquid. — Dilute sulphuric acid has no action upon it in the cold; stronger sulphuric acid dissolves it without evolution of gas; the solution mixed with water gives off a small quantity of gas and deposits a brown, flocculent powder. — Hydrochloric acid either dilute or concentrated, readily decomposes it, forming protochloride of copper and a number of gaseous products having an ethereal odour. — Nitric acid converts it into a yellow unctuous mass. — Strong acetic acid converts it, slowly in the cold, more quickly at a gentle heat, into an oily body, which encloses the still undecomposed portion of the compound and protects it from further action. — Sulphuretted hydrogen and sulphide of ammonium form sulphide of copper and other products not yet examined. — Ammonia extracts the copper, and leaves an oily substance. — Potash deepens the yellow colour of the compound, but at the same time dissolves a portion of it, forming a blue solution. — This compound is insoluble in water. Ether dissolves it very sparingly, to the amount of about 1 pt. in 10,000. Alcohol dissolves it with tolerable facility, and on evaporation yields it in the form of a yellow, non-crystalline powder. (Debus.)

			Debus.	
18 C	108	22·04	22·55	22·53
15 H	15	3·06	3·36	3·27
5 Cu	159	32·46		33·38
7 S	112	22·85	20·47	22·93
12 O	96	19·59		
$3(C^4H^5CuS^2,2CO^2)+Cu^2S$	490	100·00		

Oxyxanthate of Silver. — Precipitated in white flakes on adding nitrate of silver to a solution of the potassium-salt. The precipitate soon unites into a mass which has the consistence of plaster, and cannot be washed in the ordinary way. But by placing a small quantity of it on a filter, and keeping it suspended in water by means of a wash-bottle, it may be obtained in a state fit for analysis. It is very instable, blackening from separation of sulphide of silver, when gently heated either alone or in water. The same decomposition is produced after some time by diffused daylight, and instantly by direct sunshine. Hydrochloric, sulphuric, and nitric acid decompose it in the same manner as the lead-salt. When quickly heated alone, it cakes together into a tarry mass. Sulphide of potassium decomposes it instantly, forming sulphide of silver and oxyxanthate of potassium. (Debus.)

			Debus.
6 C	24	11·94	
5 H	5	2·49	
Ag	108	53·73	51·31
2 S	32	15·92	
4 O	32	15·92	
$C^4H^5AgS^2,2CO^2$	201	100·00	¶.

Sulphocarbonate of Ethyl. $C^5H^5S^3 = C^4H^5S,CS^2$.

SCHWEIZER (1844). *J. pr. Chem.* 32, 254.

Vinic or Ethylic Sulphocarbonate, Aethylsulfocarbonat. — Formed by the action of chloride of ethyl on sulphocarbonate of potassium:

$$C^4H^5Cl + KS,CS^2 = C^4H^5S,CS^2 + KCl.$$

One-half of an alcoholic solution of potash is completely saturated with sulphuretted hydrogen, and then mixed with the other half; the mixture saturated with sulphide of carbon, whereupon sulphocarbonate of potassium sinks to the bottom in the form of a dark red liquid; and vapour of hydrochloric ether—evolved from a mixture of alcohol, common salt and oil of vitriol, and washed with water—passed through the liquid. After the liquid saturated with hydrochloric ether has been left for several days in a stoppered bottle and frequently agitated, vapour of hydrochloric ether is again passed through it; and this series of processes is repeated several times. The greater part of the potash is gradually converted into chloride of potassium, which crystallizes out; and the decanted liquid, on being mixed with water, deposits an oily mixture of sulphocarbonate of ethyl and sulphide of carbon, which latter is very difficult to separate. For when the liquid, after being washed with water, is subjected to fractional distillation, even the last distillate is still contaminated with sulphide of carbon. This last distillate must therefore be again shaken up with aqueous potash in the cold, and this treatment repeated as long as the potash acquires a yellowish red colour from formation of sulphocarbonate of potassium.

Yellow liquid, becoming dark red when heated, but recovering its yellow colour on cooling; heavier than water. Begins to boil at 160°; but its boiling point continually rises, probably from partial decomposition

[or impurity?]. Has a sweetish alliaceous odour, and an agreeably sweet taste, like that of anise.

			Schweizer.
5 C	30	36·15	35·65
5 H	5	6·02	6·57
3 S	48	57·83	58·13
C^4H^5S,CS^2	83	100·00	100·35

When set on fire, it burns with a blue flame. — Heated with alcoholic potash, it is very quickly decomposed into sulphocarbonate of potassium and sulphide of ethyl [and carbonate of potash?]

Very slightly soluble in water; dissolves readily in alcohol and ether. (Schweizer.)

¶ Sulphoxanthic Acid. $C^4H^6S^2,C^2S^4$.

CHANCEL. *Compt. rend.* 32, 642; *Instit.* 1851, 138; *J. pr. Chem.* 53, 176; *Pharm. Centr.* 1851, 520.

Not known in the free state.

Sulphoxanthate of Potassium, $C^4H^5KS^2,C^2S^4$, is formed by treating mercaptide of potassium, $C^4H^5KS^2$, with an equivalent quantity of sulphide of carbon. Combination then takes place, attended with evolution of heat; and a white salt is formed, soluble in water and in alcohol.

6 C	24·0	14·62
5 H	5·0	3·05
6 S	96·0	58·46
K	39·2	23·87
$C^4H^5KS^2,2CS^2$	164·2	100·00

May be regarded as carbovinate of potash in which all the sulphur is replaced by oxygen, or as xanthate of potash in which the *remaining* oxygen is replaced by sulphur.

Decomposes at 100° into pentasulphide of potassium and an oil which Chancel regards as oil of garlic.

Carbonic acid gas passed through the alcoholic solution converts the salt into oxyxanthate of potassium, $C^4H^5KS^2,2CO^2$ (p. 461). A solution of sulphoxanthate of potassium forms yellow precipitates with lead-, mercury-, and silver-salts, and a crimson precipitate with copper-salts. All these precipitates decompose quickly when exposed to the air, forming metallic sulphides. The precipitate formed in a solution of cupric sulphate is a cuprous salt, whose formation is attended with that of a body composed of $C^6H^5S^6$. (Chancel.) ¶

Sulphophosphovinic Acid. $HO,C^4H^6O^2,PS^2O^3 = 2HO,C^4H^5O,PS^2O^3$.

CLOEZ (1846). *Compt. rend.* 24, 388.

Wein-Schwefelphosphorsäure, Acide sulfoxyphosphovinique. — Formed by the action of sulphoxyphosphoric acid, PS^2O^3, on alcohol.

The potash and soda-salts are easily obtained by agitating chlorosulphide of phosphorous, PS^2Cl^3, with alcoholic potash or soda. They dissolve readily in water and alcohol.

$$C^4H^6O^2 + PS^2Cl^3 + 5KO = KO,C^4H^5KO^2,PS^2O^3 + 3KCl + HO.$$

The baryta, strontia, and lime-salts, obtained by saturating the aqueous acid with the corresponding carbonates, are crystallizable. The formula of the baryta-salt is: $BaO,C^4H^5BaO^2,PS^2O^3$. (Cloez.)

Perchlorate of Ethyl. C^4H^5O,ClO^7?

CLARK, HARE, & M. BOYLE (1841). *Phil. Mag. J.* 19, 370; also *J. pr. Chem.* 26, 128.

Perchloric ether, Perchlorate of oxide of Ethyl, Ueberchorsaures Aethyloxyd, Ueberchlorvinester.

Preparation. 1 At. perchlorate of baryta is rubbed to a fine powder with 1 At. crystallized sulphovinate of baryta; a small quantity of the mixture, not exceeding 80 grains (on account of the danger of explosion), introduced into a small retort, connected with a tube-shaped receiver surrounded with ice; and heated in an oil-bath provided with a thermometer, by means of an Argand lamp, which can be quickly removed. A wooden screen, with holes filled up with thick plates of glass, is placed between the operator and the retort. No action takes place till the temperature rises to 100°; and so long as the water [of crystallization] has not passed over, there is no fear of explosion. But above 100°, the heat must be very slowly raised to 171°, at which temperature the distillation comes to an end:

$$C^4H^5BaO^2,2SO^3 + BaO,ClO^7 = 2(BaO,SO^3) + C^4H^5O,ClO^7.$$

With perchlorate of potash the preparation does not succeed; neither can the ether be obtained by the use of sulphovinic acid instead of the baryta-salt. — The perchloric ether collects in the receiver, covered with a layer of water. The water is removed—without taking the receiver in the hand, which might cause an explosion — by means of a strip of paper moistened at the end. — To preserve the perchloric ether without danger, it may be mixed with absolute alcohol; for a mixture of 1—2 parts absolute alcohol with the perchloric ether obtained from 1 pt. of sulphovinate of baryta does not explode. The pure ether may be again separated from this mixture by the addition of an equal bulk of water; the separation is however always attended with loss, because the water exerts a decomposing action on the ether. All manipulations with this compound must be performed with gloves on the hands, and a mask with thick eye-glasses before the face.

Transparent and colourless liquid, heavier than water, of agreeable odour, and sweet, afterwards bitter, cinnamon-like taste. At 100°, it either explodes or swells up.

Perchloric ether is the most violently explosive of all known compounds, the explosion being induced by heat, friction, percussion, and often taking place without any apparent cause. If the above-mentioned mixture of perchloric ether with alcohol be poured into a basin containing an equal quantity of water, the greater part of the hydrated

alcohol poured off from the drop of perchloric ether which falls to the bottom, and the remaining liquid thrown on a wet filter supported by a wire funnel, so that the watery liquid may run off,—the drop of perchloric ether which remains on the filter, may be exploded by contact with a hot body or by the blow of a hammer. The least drop exploded on an open porcelain basin crumbles it to powder. — Perchloric ether does not decompose when kept under water; but undergoes partial decomposition when separated by water from its alcoholic solution — Alcoholic potash added to the mixture of perchloric ether and alcohol, instantly produces complete decomposition of the ether, and throws down a larger quantity of perchlorate of potash.

Perchloric ether is insoluble in water; its solution in a sufficient quantity of alcohol burns away completely, when set on fire, without the least explosion. (Hare & Boyle.)

Nitrite of Ethyl. C^4H^5O,NO^3.

NAVIER & GEOFFROY. *Mém. de l'Acad. à Par.* 1742, 515.
SEBASTIANI. De nitro et modo, cum ejus acido ol. naphthæ parandi. Erf. 1746, 35.
HENKEL. De naphtha nitri, per ignem elaboranda. Erf. 1761.
BOGUES. *J. Phys.* 1773, Juni, 478.
DEHNE, BLACK. *Crell. chem. J.* 1, 44 & 50.
TIELEBEIN. *Crell. Ann.* 1784, 2, 221 and 312; 1786, 1, 37 and 150.
V. d. BALLEN. *Crell. Ann.* 1787, 1, 531.
WOULFE, PELLETIER. *J. Phys.* 1784, Dec. 21. *J. Phys.* 26, 457.
KUNSEMÜLLER. *Crell. Ann.* 1790, 1, 218 and 312.
DE LASSONE & CORNETTE, *Mém. Soc. Roy. Par.* 5, 56; also *Crell. Ann.* 1790, 2, 64.
DEVEUX, PROUST. *Ann. Chim.* 22, 144; 42, 231.
BRAGNATELLI. *A. Gehl.* 1, 579.
THÉNARD. *Mém. de la Soc. d'Arcueil.* 1, 75 and 358; abstr. *N. Gehl.* 4, 18.
BOUILLON LAGRANGE. *Ann. Chim. Phys.* 12, 109; also *J. Pharm.* 5, 433; also *N. Tr.* 5, 1, 356.
DUFLOS. *N. Tr.* 6, 2, 136. — *Berl. Jahrb.* 27, 1, 87; 28, 2, 213.
JEAN DUMAS & POL. BOULLAY. *Ann. Chim. Phys.* 37, 15; also *J. Pharm.* 14, 113; also *Schw.* 52, 337 and 433; also *Pogg.* 12, 430; also *N Tr.* 17, 2, 109.
LIEBIG. *Ann. Pharm.* 30, 142.
EMIL KOPP. *Rev. scientif.* 27, 273; abstr. *N. J. Pharm.* 11, 320.

Nitrous ether, Vinic or Ethylic Nitrite, Hyponitrous ether, Salpetrigsaures Athyloxyd, Salpetrigsaurer Aether, Salpetrigvinester, Ether hyponitreux, Ether nitreux, Nitrite d'Oxyde d'Ethyle; formerly *Nitric ether, Salpeternaphtha, Salpeteräther, Ether nitrique.* — First observed by Kunkel in 1681, and rediscovered by Navier in 1742, and by Sebastiani in 1746. Its composition was ascertained by Dumas & Boullay.

Formation. By the action of nitrous acid, and likewise of nitric or hyponitric acid on alcohol, inasmuch as the last named acids are reduced to nitrous acid by the action of a portion of the alcohol. — Respecting the doubtful formation of this compound from nitric acid and brucine, vid.

Brucine. — ¶. Mohr (*Arch. Pharm.* [2] 74, 47) doubts the existence of nitrous ether, or at all events its actual presence in the preparation known by that name, because he could not discover any signs of decomposition in that preparation (obtained by distilling alcohol with nitric acid), on distilling it with caustic potash or leaving it in contact with an alcoholic solution of potash. Strecker, however, has shown (*Ann. Pharm.* 77, 331) that nitrous ether is resolved by hydrate of potash into nitrous acid and alcohol (*vid.* p. 475).

Preparation. 1. Fuming nitric acid is mixed with alcohol in a well-closed bottle kept at a very low temperature; the evolved gas let out after a few days, by boring a hole through the cork; and the layer of nitrous ether which has risen to the top of the liquid separated by a dividing funnel. Navier & Baumé take 2 pts. nitric acid to 3 pts. alcohol; Wallerius, equal parts; Tielebein takes 3 pts. acid to 4 pts. alcohol, and separates the ether, not by the funnel, but by distillation. This process is dangerous, on account of the great liability of the vessels being burst by the gas and vapour which form.

2. Black arranges in layers, 2 pts. of fuming nitric acid, 1 pt. water, and 3 pts. alcohol, otherwise proceeding as in (1).

3. By distilling a mixture of nitric acid and alcohol. Woulfe distils fuming nitric acid with alcohol into a receiver connected with two Woulfe's bottles containing alcohol. Bogues distils dilute nitric acid with an equal quantity of alcohol. Mitouard distils 1 pt. of the fuming acid with 3 pts. of alcohol. Dehne introduces 64 pts. of alcohol into a tubulated retort provided with a wide receiver, and adds 1 pt. of fuming nitric acid every four hours, during the severest cold of winter, till 25 pts. have been added; the mixture then froths up, but without rise of temperature; he afterwards adds ½ pt. of acid twice a day till 53 pts. of acid have been used, and 51 pts. of nitrous ether have passed over. — Duflos introduces 4 pts. of 86 per cent. alcohol into a retort, and gradually pours through the tubulus, within an hour, 4 pts. of concentrated nitric acid, without application of external heat. The distillate, amounting to 4 pts. which collects in the course of 48 hours in the receiver surrounded by a freezing mixture, is agitated with an equal quantity of lime-water, and the nitrous ether which separates is rectified over half its weight of nitrate of lime; the quantity thus obtained amounts to 2½ pts. Boullay (*Bull. Pharm.* 3, 145) connects a doubly tubulated retort of 18 litres capacity with a receiver and with two Woulfe's bottles containing solution of common salt; fits into one tubulus a copper funnel provided with a stopcock, and into the other a similar funnel made of platinum; heats the retort to 60°; pours through the first tubulus 50 grms. of alcohol of 40° Bm., and through the second 50 grms. of nitric acid of 36° Bm.,— which liquids pass off almost wholly in vapour and with brisk effervescence; he then, after about a quarter of an hour, when the whole has become quiet, introduces another equal quantity of the two liquids, — and proceeds in the same manner several times. The principal portion of the nitrous ether collects above the salt solutions. A glass or platinum funnel may also be used, in which the alcohol is mixed with the acid a short time before opening the cock. Duroziez (*J. Pharm.* 9, 191; also *Repert.* 16, 251; also *Mag. Pharm.* 3, 62) mixes in a retort 48 pts. of alcohol of 36° Bm. with 24 pts. of nitric acid of 32° Bm. and then with 12 pts. oil of vitriol. In five minutes, intumescence take place spontaneously. The distillate, which passes over without any application of heat from without and amounts to 23 pts., yields, when shaken up with water, 10·5 pts. of nitrous ether. Proust introduces into a retort

connected with an empty receiver and with three Woulfe's bottles containing alcohol, 3 pts. of nitric acid of sp. gr. 1·3 and 4 pts. of alcohol, heating the mixture slightly at the beginning only; the nitrous ether, which chiefly passes over into the alcohol in the first bottle, is separated by dilute potash-ley. — Thénard heats in a retort connected with five Woulfe's bottles half filled with solution of salt and surrounded with salt and ice, a mixture of equal parts of alcohol of 35° Bm. and nitric acid of 32° Bm; whenever the action becomes too violent, he cools the retort by sprinkling water upon it, whereupon the action goes on quietly, and at length terminates spontaneously. The layers of nitrous ether floating on the salt-solution are separated by the dividing funnel. The smaller the quantity of the mixture, the better does the operation succeed, on account of the greater facility of cooling; by this process, 200 grms. of alcohol of 40° Bm. with 200 grms. nitric acid, yield between 45 and 50 grms. of purified nitrous ether. (Dumas & Boullay.) — Laplanche passes the nitric and nitrous acid vapours evolved by heating in a retort a mixture of 2 pts. nitric acid and 1 pt. oil of vitriol, into a globe containing 1 pt. of alcohol and connected with a receiver, and rectifies the liquid which passes over into the latter.

4. By distilling alcohol with sulphuric acid and a nitrate. Nitrous ether thus prepared may be contaminated with common ether. Bucholz (*A. Tr.* 14, 2, 130) distils a mixture of 16 pts. alcohol, 8 pts. nitre, and 5 pts. oil of vitriol, till 12 pts. have passed over, and separates the nitrous ether from the distillate by lime-water. Pedroni (*Compt. rend.* 17, 769; also *J. pr. Chem.* 30, 375) heats 9 pts. of alcohol with 11 pts. crystallised nitrate of ammonia and 8 pts. oil of vitriol; the mixture distils quite quietly.

5. To the mixture of alcohol and nitric acid there is added a deoxidizing substance, so that the nitric acid may be reduced to nitrous acid by this substance and not by a portion of the alcohol. Brugnatelli adds 3 pts. of fuming nitric acid to a mixture of 1 pt. sugar and 2 pts. alcohol contained in a tubulated retort, whereupon the mass boils up spontaneously, and very good nitrous ether passes over. Laudet (*Bull. Pharm.* 6, 218) mixes 1 pt. of gum arabic powder with 4 pts. alcohol of 36° Bm. and 4 pts. nitric acid of 34° Bm. in a loosely closed flask; sets the mixture aside for 24 hours, shaking it up frequently; then adapts to the mouth of the flask a bent tube leading into a bottle surrounded with a freezing mixture; and heats the mixture gently to commencing ebullition, till $\frac{2}{3}$ of the distillate are condensed; this quantity yields $1\frac{1}{3}$ pt. of pure nitrous ether. Alcohol of 40° Bm. yields a smaller quantity. According to Vallée & Boullay (*Bull. Pharm.* 6, 218) 4 pts. of alcohol yield by this process only 1 pt. of nitrous ether, but if the gum be left out, rather more, viz. $1\frac{1}{3}$ pt.; according to these chemists, the gum merely retards the action of the acid, but by no means increases the quantity of nitrous ether produced. J. Grant (*Pharm. J. Trans.* 10, 244; *Ann. Pharm.* 76, 282) adds nitric acid to a mixture of alcohol and starch, heating the mixture gently if necessary. E. Kopp introduces equal measures of alcohol and nitric acid into a distillatory apparatus, together with filings or cuttings of copper. The action never becomes violent, even when large quantities of material are used, and the distillation goes on to the end with scarcely any application of heat from without. The vapour passed first through a bottle full of water, and then through a long chloride of calcium tube, condenses in a receiver surrounded with a freezing mixture, in the form of perfectly pure nitrous ether, free from aldehyde, and

therefore not turned brown by potash. Jonas (*Arch. Pharm.* [2], 72, 9) uses iron turnings instead of copper.

6. Nitrous or hyponitric acid is made to act directly on alcohol. — Nitrous ether is immediately formed on mixing alcohol with the hyponitric acid obtained by distilling nitrate of lead. (Gay-Lussac.) — Bouillon-Lagrange mixes equal parts of alcohol of 40° Bm. and nitric acid of 36° Bm., and passes into this mixture, through the tubulus of the retort, a stream of nitrous gas evolved from nitric acid and copper. In the course of an hour and a half, the liquid becomes heated to the boiling point, and continues to boil for half an hour; the vapours are passed into Woulfe's bottles, cooled and partly filled with salt water; the nitrous ether which collects in these bottles amounts to $\frac{3}{8}$ of the mixture employed. — Liebig heats 1 pt. of starch with 10 pts. nitric acid of sp. gr. 1·32 in a capacious retort immersed in the water-bath, and passes the nitrous vapours evolved therefrom, through a knee-shaped tube to the bottom of a Woulfe's bottle, containing a cold mixture of 2 pts. of 85 per cent. alcohol and 1 pt. water. The ether vapour then passes from the second opening of the bottle through a tube 3 feet long, and cooled by wet paper, into a receiver kept at a very low temperature: the nitrous vapours, as they enter the bottle, immediately form nitrous ether, which distils over very abundantly in a continuous stream. All rise of temperature in the alcohol must be carefully prevented by cooling the Woulfe's bottle; otherwise it will begin to boil violently, and yield no more ether. The distillate is freed from alcohol by water, and from water by chloride of calcium. It is perfectly free from aldehyde, which substance is generally present in nitrous ether prepared by the other processes. [Should not hydrochloric ether be formed by the chloride of calcium? The presence of this compound would explain the low boiling point of nitrous ether prepared by this process.]

7. Nitrate of potash is acted upon in a distillatory apparatus at ordinary temperatures, by a mixture of alcohol and oil of vitriol. — Proust uses nitre which has been for the most part converted into nitrite of potash by continued fusion. — When nitrite of potash or soda is distilled with alcohol and dilute sulphuric acid, or when a mixture of these substances is set aside in a bottle surrounded with ice (as in method 1), there is produced, according to Hare (*Phil. Mag. J.* 15, 488), also *J. pr. Chem.* 19, 181), a compound ether, which he regards as different from ordinary nitrous ether. It boils at 18·3°, consequently hisses when brought in contact with the tongue or the finger, like water on red-hot iron, and produces by its spontaneous evaporation a cold of — 9° to — 18°. If heated to the boiling point, and then removed to a cooler place, it continues to boil for some time, probably in consequence of partial decomposition, by which a permanent gas is produced. When rectified over lime, it leaves in union with the lime, an oil which may be dissolved out by ether and remains behind when the ether is evaporated. [The few properties here stated as belonging to this ether, cannot be regarded as proofs of its being *essentially* different from nitrous ether, inasmuch as Liebig found the boiling point of that compound to be even lower than that just given.]

Ritter (*Scher. J.* 3, 66), in distilling a mixture of 3 pts. alcohol, 3 pts. oil of vitriol, 6 pts. nitre and 2 pts. black oxide of manganese, observed that after the nitrous ether had passed over, and the residue in the retort had become dry, a liquid distilled over, from which water precipitated a peculiar oil, viscid, heavier than water, having an unpleasant biting odour, producing a strong and persistent burning sensation on the tongue, and only slightly soluble in water [oxalic ether?].

Purification. Nitrous ether obtained by any of these methods may contain: water, alcohol, nitrous acid, nitric acid, acetic acid, acetic ether, aldehyde (in which case, according to Liebig, it imparts a dark brown colour to alcoholic potash), common ether (when oil of vitriol is used in the preparation), and perhaps also hydrocyanic acid (p. 217).—The alcohol may be removed by agitation with water or aqueous potash, the nitrous ether then rising to the surface of the liquid. — The free acids may be removed by agitation with solution of potash, the ether being then separated from the lower liquid and rectified; or, as recommended by Thénard, by frequent agitation with powdered lime (which at the same time takes up the water), till the liquid ceases to redden litmus, after which it merely requires to be decanted. — The ether may also be dehydrated by chloride of calcium, which, however, may give rise to the formation of hydrochloric ether. — No particular process is given for the removal of aldehyde (perhaps by potash, which however would be apt to decompose the nitrous ether), acetic ether or vinic ether.

Properties. Pale-yellow. — According to Couerbe, this colour arises from the presence of an oil, which may be removed by repeated distillation over sugar. Grosourdy (*J. Chim. méd.* [3,] 7, 706,) also attributes the colour to the presence of a hydrocarbon. Sp. gr. 0·886 at +4° (Dumas and Boullay); 0·947 at 15° (Liebig). Boils at 21° under a pressure of 0·758 met. (Thénard); boils at 16·4 (Liebig). Produces great cold by its evaporation, so that on pouring it on the surface of an equal volume of water, and blowing gently upon it with the mouth, the whole of the water freezes. (Liebig.) Vapour-density=2·627, (Dumas & Bouillay.) — Its odour is penetrating and ethereal; according to Liebig, very pleasant, like that of apples and Hungarian wine. Affects the head strongly when inhaled. Has a peculiar pungent taste.

			Dumas & Boullay.	Thénard. *earlier.*	Thénard. *later.*
4 C	24	32·00	32·69	39·27	28·65
N	14	18·66	19·00	16·41	14·49
5 H	5	6·67	6·85	9·59	8·54
4 O	32	42·67	41·46	34·73	48·32
C^4H^5O,NO^3	75	100·00	100·00	100·00	100·00

	Vol.	Density.
C-vapour	4	1·6640
N-gas	1	0·9706
H-gas	5	0·3465
O-gas	2	2·2186
Nitrous ether vapour	2	5·1997
	1	2·5998

Decompositions. 1. Nitrous ether turns sour when left for a considerable time in stoppered bottles containing air, and more quickly by distillation. (Thénard.) This acidification is generally attributed to the conversion of the combined nitrous acid into nitric; but according to Monheim (*Repert.* 11, 56; *Br. Arch.* 19, 122), it is wholly due to nitrous gas absorbed in the preparation of the ether, this gas being converted into nitric acid by taking up oxygen from the air. If, therefore, the *Spiritus Nitri dulcis* (mixture of nitrous ether and alcohol), be left for some time in contact with the air, or shaken up with air till it no longer takes up oxygen, and then freed from the resulting acid by means of

magnesia, it will not again become sour. According to Stoltze (*Berl. Jahrb.* 24, 2, 237), *Spiritus Nitri dulcis* turns sour even after being treated by Monheim's method; but the acidification becomes weaker the oftener the liquid is exposed to the air and deacidulated by magnesia, because by this treatment all the nitrous ether is gradually destroyed. According to Flashoff (*Br. Arch.* 1, 213; 4, 253; 7, 6), *Spiritus Nitri dulcis* may be rendered fit for keeping, by placing it for several days in contact with half its weight of black oxide of manganese — the oxygen of which supplies the place of that of the air — and removing the acid by magnesia. But according to Duflos (*Berl. Jahrb.* 27, 1, 87,) even this *spirit* turns sour, unless it has been dehydrated by distillation over chloride of calcium. — This dehydration by chloride of calcium is also recommended by Braun (*Mag. Pharm.* 33, 55); but Geiger (*ibid.*) suggested that part of the nitrous ether might be thereby converted into hydrochloric ether, and the supposition has been verified by Schmidt (*Mag. Pharm.* 36, 89), and Duflos (*Br. Arch.* 36, 279; 38, 157). Schmidt therefore agitates the *spirit* in a capacious bottle with pounded carbonate of potash, then rectifies it over strongly dried white bole, and thereby obtains a *spirit* which may be preserved without alteration in stoppered bottles filled with it, and standing in a cool place. Duflos, on the other hand, first deacidifies the *spirit* by means of finely pulverized hydrate of potash, and then dehydrates it by distillation over nitrate of lime, or better over carbonate of potash. According to Duflos, sweet spirits of nitre thus treated keeps for years, and does not redden litmus paper, except when mixed with water, which exerts a decomposing action upon it. [Possibly the liquid already contains free acid, which however does not affect litmus till mixed with water. If this be the case, we must conclude that it has hitherto been found impracticable, and perhaps is really so, to prepare *Spiritus Nitri dulcis* fit for keeping]; compare also Riegel and Winckler (*Jahrb. prakt. Pharm.* 3, 71).

2. 41·5 grammes of nitrous ether passed through a red-hot porcelain tube yield: *a.* 0·3 grm. charcoal at the entrance of the tube; — *b.* 0·5 grm. of thick oil at the entrance of the tube; — *c.* 6·48 grm. of a brown distillate, consisting of water, hydrocyanic acid, carbonate of ammonia, and a small quantity of oil; — *d.* 6·7 grm. of carbonic acid; — and *e.* 29·9 grm. or (at 18° C and 0·758 met. pressure) 33·01 litres of gas, consisting of nitrogen, nitrous gas, carburetted hydrogen, and carbonic oxide. The loss amounts to 3·57 grm. (Thénard.) — When the vapour is passed through a tube filled with spongy platinum, nitric oxide gas is produced at 400°; but at a higher temperature the products consist of water, marsh-gas, carbonic oxide, hydrocyanic acid, ammonia, and charcoal (Kuhlmann, *Ann. Pharm.* 29, 287). — 100 pts. of nitrous ether passed through a porcelain tube filled with pumice-stone, yield, when the tube is raised to a white heat, 5·3 pts. of hydrocyanic acid and 1·9 pt. ammonia; and at a dull red heat, 3·64 pts. hydrocyanic acid and 2·24 pts. ammonia. If the tube is filled with spongy platinum, the quantity of hydrocyanic acid produced is between 3·62 and 4·0 pts., and that of the ammonia between 6·12 and 8·51 pts.; and when the tube is filled with charcoal, only 0·4 — 1·11 pt. hydrocyanic acid is obtained, together with 4·96 — 4·55 pts. ammonia. (Sobrero, *N. J. Pharm.* 7, 448; also *J. pr. Chem.* 36, 16.)

3. Nitrous ether set on fire in the air burns with a clear white flame. In the glow-lamp it burns as readily as vinic ether, so that the ignition is very apt to pass into flaming combustion; during the slow combustion, it gives off, besides nitric oxide gas, vapours of a still

more suffocating and disagreeable character than those evolved by ether under similar circumstances, and containing principally acetic acid and a resinous substance which reduces metals. (Daniell & Phillips, *Gilb.* 75, 105.) Part of the resinous matter forms a coating on the colder part of the spiral; a larger portion settles upon the cap which is placed over the glow-lamp; in this also a quantity of acetic acid collects, holding some of the resinous matter in solution. This acid, when freed from undecomposed nitrous ether by distilling off one-third of its bulk, forms a light yellow, acid liquid which exhibits the characters of lampic acid, reduces mercuric acetate to the state of mercurous salt, and after neutralization with potash and careful evaporation, deposits a large quantity of resinous matter. The *resinous matter* (*hydrocarburet of azote*) is light yellow, tenacious at first, but brittle after drying, and has a harsh, bitter and unpleasant taste. According to Faraday & Daniell (*Gilb.* 75, 106), it contains 49·38 per cent. C, 26·87 N, and 23·75 H [no O ?], and is therefore $C^4NH^{11} = C^4H^8, NH^3$ [improbable ?]. It reddens turmeric; smells ammoniacal when heated; burns away very readily with hissing and sparkling [is therefore probably a nitro-compound], leaving a quantity of tumefied charcoal in the state of solution; reduces silver and gold from their salts; and produces, when gradually heated with aqueous bichloride of platinum, a kind of explosion, by which a portion of the liquid is scattered about, and metallic platinum is precipitated, together with a black powder which, after drying, explodes with flame when heated, and leaves metallic platinum. (Daniell & Phillips.) In Böttger's glow-lamp (p. 179), care being taken not to spread out the asbestus-wick too much, so that the ignition may not proceed to flaming combustion, a yellowish white resinous matter likewise collects in the cap, together with a transparent, colourless distillate which reddens litmus strongly, smells like lampic acid and nitrous ether together, assumes merely a pale yellow colour when heated with oil of vitriol, and effects the following reductions: Boiled for a long time with mercuric oxide, it reduces the greater part of that oxide to the metallic state, and dissolves a smaller quantity as mercurous oxide. Boiled with solution of corrosive sublimate, it precipitates calomel and a small quantity of metal; and when boiled with nitrate of silver, throws down all the silver in the metallic state. From chloride of gold it likewise precipitates the metal in a state of very fine division, but without gilding the vessel; but does not reduce bichloride of platinum at a boiling heat, not even on the addition of a small quantity of ammonia. (Böttger, *J. pr. Chem.* 12, 336; also *N. Br. Arch.* 13, 273.) In the asbestus glow-lamp, with chromic acid sprinkled on the wick, nitrous acid behaves like alcohol. (Böttger, p. 210.)

4. Nitrous ether froths up violently with oil of vitriol. (Brugnatelli.)

5. Left in contact for 4 years with mercuric oxide, it yields metallic mercury, and a few crystals, probably consisting of mercurous nitrate. (N. E. Henry.)

6. Hydrosulphate of ammonia acts violently upon nitrous ether, decomposing it completely in two minutes, and yielding alcohol, ammonia, water, and sulphur (E. Kopp):

$$C^4NH^5O^4 + 6(NH^3,HS) = C^4H^6O^2 + 7NH^3 + 2HO + 6S.$$

The strongly ammoniacal liquid separated from the precipitated sulphur, when neutralized with hydrochloric acid and distilled, yields alcohol having a very weak alliaceous odour, and leaves pure sal-ammoniac. (E. Kopp.)

7. The mixture of nitrous ether with alcoholic potash (which, according to Liebig, does not turn brown unless it contains aldehyde) soon deposits acetate of potash (from admixture of acetic ether) and then nitrate of potash. These two salts are also formed on agitating the nitrous ether with aqueous potash, a gas having an ethereal odour and containing nitric oxide being at the same time evolved. (Thénard.) According to Strecker (*Ann. Pharm.* 77, 231), nitrous ether is slowly decomposed by hydrate of potash, at ordinary temperatures, into nitrous acid and alcohol; the same decomposition is more speedily effected by the alcoholic solution of potash. Magnesia, ferroso-ferric oxide, iron, and copper, left in contact with the ether for 4 years in close vessels, likewise withdraw the acid from it. Phosphorus in the same time dissolves in the ether as phosphoric acid, and sulphur as sulphuric acid. (N. E. Henry, *J. Pharm.* 13, 119.)

8. Nitrous ether distilled over chloride of calcium is partly converted into hydrochloric ether (Duflos, *Br. Arch.* 38, 157):

$$C^4H^5O,NO^3 + CaCl = C^4H^5Cl + CaO,NO^3.$$

Combinations. Nitrous ether dissolves in 48 pts. of water, but with evolution of acetic and nitrous acid, especially when the water is heated. (Thénard.)

Nitrous ether of sp. gr. 0·909 dissolves $\frac{1}{20}$ pt. of sulphur; the solution has the colour of the ether, the taste and odour of sulphuretted hydrogen, blackens lead-salts, and is not precipitated by water. (Favre, *A. Gehl.* 4, 228.)

Nitrous ether mixes in all proportions with *Alcohol*, and forms with it the liquid called *Sweet Spirit of Nitre, Spiritus Nitri dulcis.* Water, the aqueous solution of neutral tartrate of potash (Funke, *Br. Arch.* 4, 265), and other aqueous solutions, separate the nitrous ether completely from this state of combination; but, according to Laudet, a saturated solution of common salt does not.

It mixes with *Glacial Acetic acid*, with *Vinic ether*, and with other ethereal liquids.

Nitrate of Ethyl. C^4H^5O,NO^5.

MILLON (1834.) *N. Ann. Chim. Phys.* 8, 233; also *J. pr. Chem.* 30, 370.

Nitric ether, Salpetersaures Aethyloxyd, Salpetervinester, Ether nitrique, Nitrate d'Oxyde d'Ethyle.

Formed by the action of nitric acid upon alcohol, when the nitrous acid produced by the oxidizing action of the acid on a portion of the alcohol is removed, as fast as it is formed, by the agency of urea. (VII, 367, 4.) This addition of nitrate of urea causes the distillation to go on quietly over the open fire, and produces a distillate consisting wholly of nitric ether, alcohol, and water. If the nitric acid contains chlorine, or if it is added in excess, *e. g.* in equal volume with the alcohol, the addition of urea is useless.

Preparation. Between 60 and 75 grm. of alcohol of 35° Bm. is distilled at a gentle heat, with an equal weight of nitric acid of sp. gr. 1·40

(or, which is about the same thing, 2 vol. alcohol to 1 vol. nitric acid), and between 1 and 2 grm. of nitrate of urea, the receiver being changed as soon as the hydrated alcohol which comes over first, is replaced by nitric ether, which may be known by its odour. The first portions of ether remain dissolved in the alcohol, but as the distillation proceeds, the ether comes over in a state of continually increasing purity, and settles in a separate layer below the alcoholic solution. The distillation is stopped as soon as the residue is reduced to $\frac{1}{8}$ of the original mixture. This residue still retains the greater part of the nitrate of urea in its original state, and on cooling, deposits it in colourless crystals, even if the original salt were strongly coloured; on this, in fact, depends the purification of urea by Millon's process. (VII, 364.) If, however, the application of heat to the residue be continued, the ordinary products of the action of nitric acid upon alcohol are evolved, with violent effervescence.

The nitric ether thus obtained is washed with aqueous potash and afterwards with water, then left for two days in contact with lumps of chloride of calcium, and finally decanted and rectified.

Properties. Liquid of sp. gr. 1·112 at 17°; boils at 85°; has an odour different from that of nitrous ether, and a very sweet taste, leaving a bitterish aftertaste.

			Millon.
5 C	24	26·37	26·55
N	14	15·38	15·17
5 H	5	5·50	5·80
6 O	48	52·75	52·48
C^4H^5O,NO^5	91	100·00	100·00

Decompositions. Nitric ether burns with a white flame when set on fire. If an attempt be made to determine its vapour-density by Dumas' method (*Ann. Chim. Phys.* 33, 141), and, after the ether has been converted into vapour, and this vapour heated somewhat above the boiling point, the blow-pipe flame be directed on the fine beak of the glass globe for the purpose of sealing it, the vapour explodes violently and bursts the globe. If, on the other hand, the globe be filled with vapour at a lower temperature, this vapour takes fire without exploding. — Chlorine and strong nitric acid decompose nitric ether; so likewise does hydrochloric acid, with formation of aqua-regia. — Oil of vitriol is capable of dissolving $\frac{1}{4}$ of its weight of nitric ether, when the ether is gradually added to it; at first, the solution of the ether takes place without any particular effect; but after a few minutes, the liquid gives off nitrous fumes, then becomes heated, evolves nitric oxide, and blackens, the whole of the nitric ether being decomposed. — Strong aqueous potash has no action on nitric ether, but alcoholic potash decomposes it at ordinary temperatures, with separation of crystals of nitre. (Millon.)

A mixture of nitric ether and ammoniacal alcohol, through which sulphuretted hydrogen is passed, becomes heated to 35° or 40°, assumes a darker colour, deposits needles of sulphur, which rapidly increase, and when distilled, after separation of the sulphur, yields ammonia and mercaptan, leaving only a trace of nitrate of ammonia:

$$C^4NH^5O^6 + 10HS = C^4H^6S^2 + NH^3 + 6HO + 8S.$$

(E. Kopp. *Rev. scientif.* 27, 273; abstr. *N. J. Pharm.* 11. 321.)

Combinations. Nitric ether is quite insoluble in water.

It dissolves *Iodine*, forming a violet solution.

It mixes in all proportions with *Alcohol*, and is precipitated from the solution by a small quantity of water. (Millon.)

¶ Ethylo-mercuric Nitrate. $C^4Hg^6N^2O^{12} = C^4Hg^5O,NO^5 + HgO,NO^5$.

SOBRERO & SELMI. *Compt. rend.* 33, 67; *Instit.* 1851, 234; *Rev. scientif.* [4], 1, 27; *Ann. Pharm.* 80, 108; *J. pr. Chem.* 53, 382; *Pharm. Centr.* 1851, 635; *Jahresber.* 1851, 506; *Chem. Soc. Qu. J.* 5, 86.

GERHARDT. *Ann Pharm.* 80, 11; *Rev. scientif.* [4], 1, 29; *J. pr. Chem.* 55, 43; *Jahresber.* 1851, 507; *Chem. Soc. Qu. J.* 5, 88.

Vino-mercuric Nitrate, Salpetersaures Aethyl-Quecksilberoxyd. — First obtained by Sobrero & Selmi; more minutely examined by Gerhardt.

Obtained by mixing alcohol with a very strong solution of mercuric nitrate. No precipitate is formed in the cold; but on heating the liquid, a white crystalline compound separates, even before the boiling point is attained, and its formation continues without further application of heat. (Vid. p. 256.)

White crystalline salt, which, when examined by the microscope, exhibits a highly characteristic form, consisting of six-pointed stars or hexagonal tables, shaded on the edges in such a manner that similar stars appear within them, with their vertices projecting into the angles of the tables. The crystals contain 2 At. water.

$$2(3HgO,NO^5) + C^4H^6O^2 = C^4Hg^6N^2O^{12} + 6HO.$$

The alcoholic mother-liquor contains a large quantity of mercurous nitrate. A mercurous salt also frequently separates in small needles after the new salt has been removed by decantation. The formation of mercurous salt probably depends upon secondary actions; for a mixture of alcohol and corrosive sublimate gives off a strong odour of aldehyde when heated, though the action is not accompanied by any evolution of gas.

Crystallized: dried over oil of vitriol.			Gerhardt.
4 C	24	3·1	2·9
2 H	2	0·3	0·3
6 Hg	600	78·3	78·4
2 N	28	3·3	3·6
14 O	112	15·0	14·8
$C^4Hg^5O,NO^5 + HgNO^5 + 2Aq.$	766	100·0	100·0

The salt heated in a small tube decomposes suddenly and explosively, but without detonation. — Hydrochloric acid dissolves it completely, without leaving a trace of calomel; hence it is a mercuric and not a mercurous salt. The hydrochloric acid solution gives a yellow precipitate with potash. — Sulphuretted hydrogen decomposes the salt, forming sulphide of mercury and a substance having the odour of mercaptan. Hence, in determining the mercury, the organic matter must be first destroyed by boiling the salt in aqua-regia, then evaporating to dryness, and digesting the residue in water; if this precaution be neglected, the precipitated sulphide is impure, and the mercury comes out 1 or 2 per cent. too much. — A strong aqueous solution of potash turns the salt grey; when boiled with the same solution, it turns black, but is not completely decomposed; the black substance is always

mixed with crystals, however long the boiling may be continued. Hydrochloric acid does not dissolve this black substance, though it forms but a small quantity of calomel. It appears, therefore that the salt is essentially altered by the action of potash. — Ammonia acts upon it in a similar manner.

Ethylomercuric nitrate is insoluble both in water and in alcohol.

Gerhardt is of opinion that the detonating compound which Sobrero & Selmi obtained by adding alcoholic potash to an alcoholic solution of corrosive sublimate (*vid.* p. 255) is an oxide of mercury and ethyl, $C^4Hg^6O^2$, or alcohol in which the hydrogen is replaced by mercury. Gerhardt, however, did not succeed in preparing this compound. Werther and Bruckner (*J. pr. Chem.* 55, 253, 254) were also unsuccessful in their endeavours to obtain it. ¶

Disilicate of Ethyl. $2C^4H^5O,SiO^2$.

EBELMEN, *N. Ann. Chim. Phys.* 6, 144; also *Ann. Pharm.* 57, 331; also *J. pr. Chem.* 37, 357; abstr. *Compt. rend.* 19, 398; also *N. J. Pharm.* 6, 262; also *J. pr. Chem.* 33, 417.

Bibasic Silicate of Ethyl, Ethylic Disilicate, Bibasic Silicic ether, Halb-Kieselvinester, Einfach-Kieselsaures Aethyloxyd, Protosilicate ethylique. — The three varieties of silicic ether were all discovered by Ebelmen in 1844.

Formation. Absolute alcohol, gradually added to chloride of silicium, evolves hydrochloric acid gas with violence and great *depression* of temperature, this action going on till the quantity of alcohol added somewhat exceeds that of the chloride of silicium; if the addition of alcohol be still continued, the mixture becomes heated, and evolves no more gas. If on the contrary the chloride of silicium be carefully added to the alcohol, the mixture becomes heated at first, but on further addition of chloride of silicium, cooling takes place. When such a mixture is distilled, ethylic disilicate passes over between 160° and 180°, and there remains a small residue, the quantity of which is less in proportion as the alcohol is more nearly absolute. This residue, when more strongly heated, gives off between 180° and 300°, a mixture of bibasic and monobasic silicic ether, the proportion of the latter continually increasing, so that between 300° and 350° scarcely anything but the monobasic ether is obtained. Equation for the formation of the bibasic ether;

$$2C^4H^6O^2 + SiCl^2 = 2C^4H^5O,SiO^2 + 2HCl.$$

In this reaction, therefore, 2 At. or 92 parts of alcohol, act upon 1 At., or 85·8 pts., chloride of silicium. If a somewhat small quantity of alcohol be at first added to the chloride of silicium, nothing but hydrochloric acid is evolved; but when more alcohol is added, hydrochloric ether is also produced [by the action of the hydrochloric acid on the excess of alcohol.]

Preparation. Somewhat more than 92 pts. of absolute alcohol is gradually added to 86 pts. of chloride of silicium; the mixture distilled in a retort provided with a thermometer, whereupon a large quantity of

Monosilicate of Ethyl. C^4H^5O,SiO^2.

EBELMEN. *N. Ann. Chim. Phys.* 16, 149.

Ethylic Monosilicate, Monobasic Silicate of Ethyl, Monobasic Silicic ether, Einfach-kieselvinester; Zweifach Kieselsaures Aethyloxyd, Bisilicate éthylique.

Formation. *Vid.* Formation of the bibasic compound (p. 478). For the production of this compound, a small quantity of water is necessary, besides the alcohol and chloride of silicium; *viz.* 1 At. (85·8 pts.) chloride of silicium, 1 At. (46 pts.) alcohol, and 1 At. (9 pts.) water:

$$C^4H^6O^2 + SiCl^2 + HO = C^4H^5O,SiO^2 + 2HCl.$$

With a smaller quantity of water, the bibasic compound is produced. — A small quantity of water converts the bibasic into the monobasic ether. (p. 479.)

Preparation. 86 pts. of chloride of silicium are gradually mixed with 55 pts. of 85 per cent. alcohol (whereupon hydrochloric acid gas is evolved), and the clear mixture distilled in a retort provided with a thermometer. The small quantity of distillate obtained below 350°, is a mixture of the bibasic and monobasic silicates of ethyl; but, above 350°, at which temperature the receiver should be changed, the monosilicate distils over alone, and nothing is left in the retort but a small quantity of nearly colourless, tumefied silica. The liquid which has distilled over above 350°, is rectified to dryness, a fresh receiver being put on as soon as the boiling point has risen to 350°; the distillate obtained from that point upwards is the pure monosilicate of ethyl.

Properties. Transparent, colourless liquid, much less mobile than the disilicate. Sp. gr. 1·079 at 24°. Boils constantly at 350°. Has but a faint odour, and a taste quite different from that of the disilicate.

			Ebelmen.
4 C	24	35·30	36·30
5 H	5	7·35	7·75
O	8	11·76	12·00
SiO^2	31	45·59	43·95
C^4H^5O,SiO^2	68	100·00	100·00

Decompositions. 1. Monosilicate of ethyl requires a much stronger heat to set it on fire than the disilicate. — 2. Water, without dissolving it, slowly converts it into alcohol and silicic acid. If this transformation is produced by the moisture of the air, the silica exhibits the same resemblance to Hyalite and Hydrophane as the disilicate formed under similar circumstances (p. 479). — A very small quantity of water converts this compound into bisilicate of ethyl.

Combinations. Monosilicate of ethyl mixes in all proportions with *alcohol* and *ether*.

Bisilicate of Ethyl. $C^4H^5O,2SiO^2$.

EBELMEN (1846). *N. Ann. Chim. Phys.* 16, 152.

Ethylic Bisilicate, Zweifach-Kieselvinester; Vierfach-Kieselsaures Aethyloxyd, Quadrisilicate éthylique.

Formed by adding to monosilicate of ethyl, or to the mixture of monosilicate and disilicate which passes over between 180° and 300° (p. 478), a small quantity of hydrated alcohol (rather too little than too much), and distilling the mixture at an increasing heat. After the monosilicate has passed over, at and above 360°, the residue is still further heated till it becomes viscid, so that the bubbles of vapour rise but slowly through it. This residue is the bisilicate of ethyl. If the heat applied is not strong enough, a certain quantity of monosilicate of ethyl remains mixed with it; too strong a heat, on the other hand, causes an admixture of free silica. As the exact degree of heat required is difficult to ascertain, it is best to prepare only 3 or 4 grammes of the compound at a time.

The fused mass solidifies on cooling, and forms a yellowish transparent glass having a conchoïdal fracture. It scarcely softens at 100°, but melts at a higher temperature; and when still more strongly heated, froths up, and is resolved into monosilicate of ethyl and a residue of silica.—Soluble in alcohol and ether, and in disilicate and monosilicate of ethyl. (Ebelmen.)

			Ebelmen.
4 C	24	24·24	24·7
5 H	5	5·05	5·1
O	8	8·08	8·3
2 SiO^2	62	62·63	61·9
C^4H^5O,SiO^2	99	100·00	100·0

If the bisilicate of ethyl contains monosilicate, it is soft at ordinary temperatures, and may be drawn out into threads. (Ebelmen.)

Arseniovinic Acid?

FELIX D'ARCET. *J. Chim. méd.* 12, 11; also *Ann. Pharm.* 19, 202.

When arsenic acid is treated with alcohol in the same manner as phosphoric acid is treated for the preparation of phosphovinate of baryta, a salt is obtained, containing 54·6 p. c. arseniate of baryta or 27·20 p. c. barium, 15·31 arsenic, 19·21 carbon, 3·3 hydrogen, and 34·95 oxygen. From this analysis, d'Arcet, by an inaccurate calculation of the arsenic and oxygen, obtains the improbable formula (according to the atomic weights used in this work): $BaO,C^8H^{10}O^3AsO^5$. — The analysis rather leads to the empirical formula: $2BaO,AsO^5C^{16}H^{16}O^{14}$, which, if correct, shows that the acid in question bears no analogy to phosphovinic acid.

Formiate of Ethyl. $C^6H^6O^4 = C^4H^5O,C^2HO^3$.

SEB. BUCHOLZ. *Crell. N. Entdeck.* 6, 55.
GEHLEN. *Schw.* 4, 18.
DÖBEREINER. *Gilb.* 74, 416; also *Schw.* 38, 362. — *Ann. Pharm.* 3, 145.
LIEBIG. *Ann. Pharm.* 16, 170; 17, 70.
R. F. MARCHAND. *J. pr. Chem.* 16, 430.
LÖWIG & WEIDMANN. *Pogg.* 50, 111.
HERMANN KOPP. *Ann. Pharm.* 55, 180.

Formic Ether, Ethylic Formiate, Vinic Formiate, Ameisensaures Aethyloxyd, Ether formique, Formiate éthylique. — First prepared by Seb. Bucholz in 1782.

Preparation. 1. A mixture of equal parts of highly rectified spirit and concentrated formic acid, distilled after several days' digestion, yields a distillate from which water separates a quantity of formic ether amounting to half the alcohol. (Bucholz.) — Gehlen proceeds in a similar manner; viz., by distilling to dryness a mixture of equal parts of absolute alcohol and concentrated formic acid, prepared according to his method (VII, 271, ζ); rectifies the distillate, collecting the greater portion; and separates the formic ether from the distillate by dilute potash. The formic ether thus obtained amounts to $\frac{1}{4}$ of the alcohol used, and is purified by rectifying it a second time till somewhat more than the half has passed over. — The strongest formic acid, $C^2H^2O^4$, yields a large quantity of formic ether when distilled with alcohol. (Liebig.) — 2. By distilling 7 pts. of dry formiate of soda with a mixture of 6 pts. of highly rectified spirit and 10 pts. oil of vitriol; agitating the distillate, if acid, with magnesia; separating it from alcohol by agitation with water; then decanting the ether and rectifying it over chloride of calcium. (Döbereiner.) — On mixing the three ingredients, heat is evolved sufficient to distil over all the formic ether. The distillate is agitated with an equal volume of milk of lime, and the formic ether evolved as above is dehydrated by chloride of calcium, after separation from the lower stratum, the chloride of calcium being renewed as often as it becomes moist, after which the ether is simply decanted off. (Liebig.) — H. Kopp uses 8 pts. of formiate of soda to 7 pts. of 88 per cent. alcohol and 11 pts. oil of vitriol; conducting the process in other respects in the same manner as Liebig. — 3. A mixture of 30 pts. oil of vitriol, 15 pts. water, and 15 pts. highly rectified spirit is poured upon an intimate mixture of 10 pts. starch and 37 pts. very finely pounded manganese, and the whole distilled with gentle ebullition as long as formic ether continues to pass over. A large quantity of chloride of calcium is then dissolved in the distillate, whereby in the following distillation over the water-bath, the greater part of the water and alcohol is retained, and the liquid which passes over is again rectified with chloride of calcium.

Properties. Thin, transparent, and colourless liquid, of sp. gr. 0·9157 at 18° (Gehlen); 0·9188 at 17°; 0·9984 at 0° (H. Kopp); 0·9577 at 0° (Pierre); boils at 54° (R. Marchand); at 56°, under a pressure of 27·7" (Döbereiner); at 55·3° with platinum wire immersed in it (H. Kopp);

according to a later determination by Kopp, at 54·9°; at 52·9°, under a pressure of 0·752 met. (Pierre); at 54·3°, under a pressure of 0·762 met. (Andrews.) — Index of refraction 1·3570. (Delffs, *Pogg.* 81, 470.) Tension of the vapour at 23°=8·2″. (Döbereiner.) Vapour-density =2·593. (Liebig.) — Has a strong and agreeable odour, like that of peach-kernels. (Bucholz.) Taste pleasant at first, like that of peach-kernels, but afterwards very strong, like that of ants. (Gehlen.)

			R. Marchand.	H. Kopp.
6 C	36	48·65	48·87	48·00
6 H	6	8·11	8·23	8·32
4 O	32	43·24	42·90	43·68
C^4H^5O,C^2HO^3	74	100·00	100·00	100·00

	Vol.	Density.
C-vapour	6	2·4960
H-gas	6	0·4158
O-gas	2	2·2186
Vapour of Formic ether	2	5·1304
	1	2·5652

Decompositions. — 1. Formic ether burns with a blue flame, whitish yellow at the points and edges. (Gehlen.) — 2. Chlorine gas passed through it is absorbed without evolution of heat; the ether then begins, after two hours, to evolve large quantities of hydrochloric acid mixed with formic acid and chloride of ethyl; and after the passage of the gas has been continued for 40 hours, heat being applied towards the end, it is converted, first into terchlorinated formic ether, $C^6Cl^3H^2O^4$, and then into perchlorinated formic ether, $C^6Cl^6O^4$. (Malaguti, Cloez.) — 3. In contact with water, aqueous alkalis, or carbonate of potash, formic ether is gradually resolved into formic acid and alcohol. (Döbereiner.)

The solution of formic ether in highly rectified spirit remains permanent. (Döbereiner); dry ammoniacal gas passed through it exerts no action. (Liebig.) — Formic ether in contact with sodium at ordinary temperatures, slowly gives off carbonic oxide gas and leaves a residue consisting principally of alcohol. If sodium be added to it as long as the evolution of carbonic oxide continues, the residue yields alcohol by distillation, without previous addition of water; but when the evolution of alcohol ceases, a considerable quantity more may be obtained by adding water. Ultimately there remains a yellowish alkaline liquid, which, when mixed with dilute hydrochloric acid, deposits a few brown resinous flakes and yields formic acid by distillation. Part of the formic ether is resolved into alcohol and carbonic oxide:

$$C^6H^6O^4 = C^4H^6O^2 + 2CO;$$

another portion is converted by the soda produced in the action [whence does this soda derive its oxygen?] into ethylate and formiate of soda, and the latter unites with a third portion of the formic ether. (Löwig & Weidmann.) [Had the formic ether used in this experiment been carefully freed from alcohol? The matter requires further investigation.]

Combinations. — Formic ether requires 18 pts. of *Water* at 9° to dissolve it. (Gehlen.)

It is precipitated from its solution in *Alcohol* by water. (Bucholz.) When *Spiritus Formicarum* is prepared by distilling ants with 30 per

cent. alcohol, no formic ether is obtained; but if the ants are immersed for half a year in 75 per cent. alcohol, the liquid then mixed with a third part of water and distilled, the compound ether is produced. (Reinsch, *Jahrb. prakt. Pharm.* 3, 95.)

Formic ether likewise mixes in all proportions with *Wood-spirit*, *Ether*, and many *Oils* both *fixed* and *volatile*. (Liebig, *Chim. org.*)

Acetate of Methyl. $C^6H^6O^4 = C^2H^3O,C^4H^3O^3$.

DUMAS & PÉLIGOT (1835). *Ann. Chim. Phys.* 58, 46; also *Ann. Pharm.* 15, 34; also *J. pr. Chem.* 3, 386.
WEIDMANN & SCHWEIZER. *Pogg.* 43, 593. — *J. pr. Chem.* 23, 39.
H. KOPP. *Ann. Pharm.* 55, 181.

Methylic Acetate, Acetate of Methylene, Essigsaures Methylen, Essigsaures Methyloxyd, Essigsaurer Holzäther, Essigformester, Acetate de Méthylène, Acetate méthylique. — Occurs in crude wood-vinegar (Weidmann & Schweizer). — Druggists sell a liquid called *Aether lignosus* s. *Spiritus pyroaceticus*, which appears to be impure acetate of methyl. It is yellowish; of sp. gr. 0·835; boils at 60°—70°; smells and tastes of acetic ether and wood-vinegar; leaves when evaporated, an empyreumatic oil smelling of creosote and garlic; burns with a white flame, and forms a turbid mixture with water, in consequence of containing oil. (Frederking, *N. Br. Arch.* 43, 1.)

Preparation. — 1. Two pts. of wood-spirit are distilled with 1 pt. of glacial acetic acid and 1 pt. oil of vitriol; the distillate shaken up with chloride of calcium, whereupon the acetate of methyl rises to the top; this product freed from sulphurous acid by agitation with quicklime, and from wood-spirit by 24 hours' contact with chloride of calcium, which takes up the latter substance. (Dumas & Péligot.) — 2. When 1 part of wood-spirit is distilled with 1 pt. acetate of potash and 2 pts. oil of vitriol, acetate of methyl passes over first, then sulphurous acid, acetic acid, methol, and a small quantity of methylic sulphate. The first receiver must therefore be removed as soon as sulphurous acid begins to escape; its contents shaken up with water; and the separated ether rectified over chloride of calcium and quicklime. (Weidmann & Schweizer.) 3. A mixture of 3 pts. wood-spirit, 14½ pts. dehydrated acetate of lead, and 5 pts. oil of vitriol is distilled; the distillate shaken up with milk of lime; the stratum of methylic acetate which rises to the surface, dehydrated by repeated treatment with chloride of calcium, then decanted from the lower liquid, and rectified. (H. Kopp.)

Properties. — Colourless liquid, of sp. gr. 0·919 at 22°; boils at 58° under a pressure of 0·762 met. Vapour-density 2·563; has a very agreeable odour, like that of acetate of ethyl. (Dumas & Péligot.) The ether completely freed from chloride of calcium by repeated distillation has a density of 0·0085 at 21°; 0·9562 at 0°, and with platinum wire immersed in it, boils at 55° (H. Kopp); according to a later determination by Kopp (*Pogg.* 72, 1, and 223), the boiling point is 56·3°. According to Pierre (*N. Ann. Chim. Phys.* 15, 325) the sp. gr. at 0° is 0·8668; the boiling point 59·5°, under a pressure of 0·7612 met. According to Andrews (*Chem. Soc. Qu. J.* 1, 27), the boiling point is 55° at 0·762 met. — Index of refraction 1·3576. (Delffs, *Pogg.* 81, 470.)

brown towards the end of the reaction, is distilled, nothing but undecomposed methylic acetate passes over at first, and then on addition of water, more methylic acetate together with methylic alcohol; the residual liquid contains a potash-salt which possesses reducing powers, and is very easily converted into acetate of potash by absorption of oxygen. (Weidmann & Schweizer.)

Methylic acetate dissolves with tolerable facility in *Water*. The solution suffers but little decomposition even by boiling.

Cyanide of Ethyl. $C^6H^5N = C^4H^4,C^2N = C^4H^4,C^2NH$.

PELOUZE (1834). *J. Pharm.* 20, 399; abstr. *Ann. Pharm.* 10, 249.

FRANKLAND & KOLBE. *Ann. Pharm.* 65, 288; *J. pr. Chem.* 42, 313; 46, 301; *Phil. Mag. J.* 31, 266; *Chem. Soc. Mem.* 3, 386; *Pharm. Centr.* 1847, 810; *N. J. Pharm.* 14, 294. — Decomposition by Potassium. *Ann. Pharm.* 65, 269; *Chem. Soc. Qu. J.* 1, 60; *Pharm. Centr.* 1848, 369.

DUMAS, MALAGUTI, AND LEBLANC. Action of Potash on Cyanide of Ethyl. *Compt. rend.* 25, 781; *Ann. Pharm.* 74, 329; *Pharm. Centr.* 1848, 95.

Hydrocyanic ether, Hydrocyanäther, Cyanwasserstoffäther, Cyanäthyl, Cyan-Vinafer, Cyanure d'Ethyle.

Preparation. 1. Sulphovinate of baryta is distilled at a gentle heat with an equal weight of cyanide of potassium, the distillate washed with four or five times its bulk of water, to remove alcohol and hydrocyanic acid, then heated for a while to 60° or 70°, and rectified over chloride of calcium (Pelouze):

$$C^4H^5BaO^2,2SO^3 + C^2NK = KO,SO^3 + BaO,SO^3 + C^4H^4,C^2N.$$

Or: Sulphovinate of potash is distilled with cyanide of potassium, and the yellow distillate mixed with water, separated therefrom by chloride of sodium, dried over chloride of calcium, and rectified. (Frankland & Kolbe.) — 2. By distilling a mixture of oxalic ether and finely pulverised cyanide of potassium. (Löwig.) — [Might also be obtained by distilling propionate of ammonia with anhydrous phosphoric acid, just as cyanide of methyl is obtained from acetate of ammonia (p. 60).]

Properties. Colourless liquid of sp. g. 0·78. Boils at 82°. Has a very powerful alliaceous odour, and is very poisonous. (Pelouze.) Sp. gr. 0·7889 at 12·6°. Boils at 88°. Smells very much like cacodyl. (Frankland & Kolbe.)

			Frankland & Kolbe.
6 C	24	65·45	65·19
5 H	5	9·09	9·46
N	14	25·46	
C^4H^4,C^2N	43	100·00	

Decompositions. Decomposed only by strong caustic potash, and even by that but slowly. Does not form a cloud with a nitrate of silver. (Pelouze.) ¶ 1. Boiled with aqueous potash in a retort in such a manner that the liquid which evaporates may be condensed and run back again, it is converted into propionate of potash, with evolution of ammonia. (Dumas, Malaguti & Leblanc; Frankland & Kolbe):

$$C^6H^5N + KO + 3HO = C^6H^5KO^4 + NH^3.$$

2. Similarly with weak *sulphuric acid* (1 pt. acid to 2 pts. water), the products being propionic acid and sulphate of ammonia (Frankland & Kolbe):

$$C^6H^5N + HSO^4 + 4HO = C^6H^6O^4 + NH^4,SO^4.$$

Potassium decomposes cyanide of ethyl at ordinary temperatures, forming cyanide of potassium and eliminating a gas which has the composition C^2H^3 or C^4H^6, and was first supposed by Frankland and Kolbe to be methyl, but was afterwards found by Frankland to be hydride of ethyl, C^4H^5,H (*vid.* VII, 171, 172, 247; VIII, 170). At the same time, the potassium is converted into a tenacious, yellowish mass, which when treated with water, yields a solution of cyanide of potassium, and leaves *Kyanethine*, a body polymeric with cyanide of ethyl, and having the composition $C^{18}H^{15}N^3$. This substance is white, inodorous, nearly tasteless, melts at 190°, boils with partial decomposition at 280°, dissolves readily in alcohol, and sparingly in cold water. It has an alkaline reaction, is scarcely acted on by potash, but dissolves, forming crystallizable salts from which the base may be precipitated in its original state by alkalis and alkaline carbonates. The quantity of kyanethine formed in the reaction of potassium on cyanide of ethyl is very small; and nothing is known about the conditions which are necessary for its production, further than that it is formed when the cyanide is dropped upon the potassium, but not when the potassium is thrown into the liquid. It is not altered by heating it to 240° in a closed tube with dry cyanide of potassium. (Frankland & Kolbe.) ¶

Combinations. Cyanide of ethyl is very slightly soluble in water, but mixes in all proportions with alcohol and ether. (Pelouze.) Dissolves with tolerable facility in water, but separates out again and rises to the surface on the addition of common salt. (Frankland & Kolbe.)

¶ Cyanate of Ethyl. $C^6H^5NO^2 = C^4H^5O,C^2NO = C^2N(C^4H^5)O^2$.

WURTZ. *Compt. rend.* 27, 241; *Laur. & Gerh. C. R.* 1849, 117; *Jahresber*, 1848, 691. — Further: *Compt. rend.* 37, 180.

Cyanic ether, Cyanäther, cyansaures Aethyloxyd, Ether cyanique.

Preparations. Cyanate of potash subjected to dry distillation with sulphovinate of potash, yields a mixture of cyanic and cyanuric ethers:

$$C^2NKO^2 + C^4H^5KO^2,2SO^3 = C^2N(C^4H^5)O^2 + 2(KO,SO^3).$$

The cyanic ether is easily separated by distillation, being very volatile, whereas the cyanuric ether (which is polymeric with it, and has a treble atomic weight) does not boil till raised to a very high temperature. It may be purified by several rectifications over chloride of calcium.

Properties. Transparent, colourless, very mobile liquid, lighter than water, and having a very high refracting power. Vapour-density 2·4. The vapour is extremely irritating, and excites a copious flow of tears.

					Vol.	Density.
6 C	24	40·68		C-vapour	6	2·4960
5 H	5	8·47		H-gas	5	0·3465
N	14	23·73		N-gas	1	0·9706
2 O	16	27·12		O-gas	1	1·1093
$C^2N(C^4H^5)O^2$	59	100·00			2	4·9224
					1	2·4612

Decompositions. 1. Cyanic ether is decomposed by *Water*, carbonic acid being evolved, and a crystalline body, $C^{10}H^{12}N^2O^2$, being formed, which may be purified by solution in water or alcohol:

$$2C^4H^5NO^2 + 2HO = 2CO^2 + C^{10}H^{12}N^2O^2.$$

The crystalline body is diethylurea [$C^{10}H^{12}N^2O^2 = C^2N^2(H^2Ae^2)O^2$].

2 Cyanic ether dissolves in aqueous ammonia, with evolution of heat. The solution, when evaporated, yields a body which crystallizes in beautiful prisms, melts when heated, dissolves in water and alcohol, and gives off ammonia when boiled with potash. It is composed of $C^6H^8N^2O^2$, and therefore contains the elements of cyanic ether, together with those of ammonia:

$$C^6H^8N^2O^2 = C^6H^5NO^2 + NH^3.$$

3. Cyanate of ethyl boiled with hydrate of potash, yields ethylamine and carbonate of potash (VII, 179).

$$C^4H^5O,C^2NO + 2(KO,HO) = 2(KO,CO^2) + C^4H^7N.$$

4. When cyanic ether is mixed with monohydrated acetic acid, carbonic acid is evolved and *ethylacetamide* produced:

$$\underbrace{\left.\begin{matrix}C^4H^3O^2\\H\end{matrix}\right\}O^2}_{\text{Acetic acid.}} + \underbrace{C^4H^5O,C^2NO}_{\text{Cyanic ether.}} = 2CO^2 + \underbrace{N\left\{\begin{matrix}C^4H^5\\C^4H^3O^2\\H\end{matrix}\right.}_{\text{Ethylacetamide.}}$$

5. Cyanic ether heated in a sealed green glass tube to 180°, with anhydrous acetic acid (p. 334), yields carbonic acid and ethylo-diacetamide:

$$\underbrace{\left.\begin{matrix}C^4H^3O^2\\C^4H^3O^2\end{matrix}\right\}O^2}_{\text{Anhydrous acetic ether.}} + \underbrace{C^4H^5O,C^2NO}_{\text{Cyanic ether.}} = 2CO^2 + \underbrace{N\left\{\begin{matrix}C^4H^5\\C^4H^3O^2\\C^4H^3O^2\end{matrix}\right.}_{\text{Ethylo-diacetamide.}}$$

6. With alcohol, cyanic ether forms ethylurethane, $C^{10}H^{11}NO^4$, without evolution of carbonic acid:

$$C^4H^6O^2 + C^6H^5NO^2 = C^{10}H^{11}NO^4.$$

Ether does not act upon cyanate of ethyl, even when strongly heated with it in sealed tubes for several days. (Wurtz, *Compt. rend.* 37, 180.)

Cyanate of Methyl, C^2H^3O,C^2NO, is obtained in a similar manner by subjecting to dry distillation a mixture of cyanate and sulphomethylate of potash. — It is very volatile, and its reactions are similar to those of cyanate of ethyl. With ammonia it forms a crystallizable compound = $C^4H^6N^2O^2$. With water it gives off carbonic acid and forms a crystallizable body = $C^6H^8N^2O^2$, which is isomeric with the product obtained by the action of ammonia on cyanate of ethyl. Distilled with potash, it yields methylamine. (Wurtz.) ¶

Sulphocyanide of Ethyl. $C^6H^5NS^2 = C^4H^4,C^2NHS^2 = C^4H^5S,C^2NS$.

CAHOURS. *N. Ann. Chim. Phys.* 18, 264; also *Ann. Pharm.* 61, 99; abstr. *Compt. rend.* 21, 365.
LÖWIG. *Pogg.* 67, 191.

Hydrosulphocyanic ether, Schwefelcyanwassenstoffäther, Schwefelcyanäthyl, Schwefelcyan-vinafer, Sulfocyanure d'Ethyle. — Discovered by Cahours in 1845.

Preparation. 1. Equal parts of sulphovinate of baryta (or lime, according to Muspratt) and sulphocyanide of potassium in the state of concentrated aqueous solution are distilled together, and the yellowish distillate washed with water, digested with chloride of calcium, and carefully rectified. (Cahours):

$$C^4H^5BaO^2,2SO^3 + C^2NKS^2 = KO,SO^3 + BaO,SO^3 + C^6H^5NS^2.$$

—2. A concentrated aqueous solution of sulphocyanide of potassium is saturated with hydrochloric ether; the mixture set aside, whereupon it decomposes slowly in diffused daylight, more quickly in sunshine, with deposition of chloride of potassium; the liquid mixed with an equal quantity of water and distilled; the distillate mixed with twice its volume of pure vinic ether; a sufficient quantity of water added to separate the vinic ether which holds the sulphocyanide of ethyl in solution; and this ethereal mixture distilled, the receiver being changed after a while, because the vinic ether passes over first. The last portion of the distillate yields, when distilled with water, a watery liquid in which the sulphocyanide of ethyl floats about in drops; and, on dissolving a small quantity of chloride of calcium in the liquid, these drops unite and form a stratum on the surface. The sulphocyanide of ethyl is decanted, placed for a few days in contact with chloride of calcium, then poured off and rectified. (Löwig.)

$$C^2NKS^2 + C^4H^5Cl = C^6H^5NS^2 + KCl.$$

The liquid which Liebig (*Pogg.* 15, 559) obtained by distilling sulphocyanide of potassium with alcohol and oil of vitriol, and regarded as sulphocyanide of ethyl, appears from his later experiments (*Ann. Pharm.* 11, 18) to contain no nitrogen, but rather to be bisulphide of ethyl, or some such compound, mixed with sulphide of carbon.

Properties. Transparent and colourless liquid, of sp. gr. 1·020 at 16° (Cahours); 1·000 at 15°, so that drops of it remain suspended in water without rising or sinking. Mobile. (Löwig.) Boils at 146° (Cahours); at about 100°. (Löwig.) Vapour density 3·018. (Cahours.) Smells like sulphocyanide of methyl (p. 121.) (Regnault.) Has a penetrating odour, like that of mercaptan, and a sweet taste, like that anise. (Löwig.)

			Cahours.	Löwig.
6 C	36	41·38	41·52	41·20
5 H	5	5·74	5·82	6·13
N	14	16·09	16·17	
2 S	32	36·79		36·25
C^4H^5,C^2NS^2	87	100·00		

	Vol.	Density.
C-vapour	6	2·4960
H-gas	5	0·3465
N-gas	1	0·9706
S-vapour	½	2·2186
Vapour of C^4H^5,C^2NS^2	2	6·0317
	1	3·0158

Decompositions. Sulphocyanide of ethyl behaves with reagents in a similar manner to sulphocyanide of methyl (p. 121); it is violently attacked by chlorine and bromine, and yields crystalline products with the latter. (Cahours.) — Nitric acid exerts a violent decomposing action upon it, but produces only a small quantity of sulphuric acid. (Löwig.) — ¶ Tolerably concentrated nitric acid acts strongly on sulphocyanide of ethyl, giving off nitrous acid, nitric oxide, and carbonic acid, and forming sulphuric acid (the quantity of which increases with the strength of the nitric acid used) and ethylosulphurous acid, $C^4H^6S^2O^6$, which on evaporating the liquid, remain in the form of an oily liquid resembling oil of vitriol and having an alliaceous odour (Muspratt, *compare* p. 407). ¶ — Sulphocyanide of ethyl is not perceptibly decomposed by boiling with aqueous potash, even for a long time; but when boiled with alcoholic potash, it gives off ammonia and bisulphide of ethyl, and leaves carbonate of potash, but not a trace of sulphocyanide of potassium. (Löwig.) [Should not mercaptan be formed rather than bisulphide of ethyl? $C^6H^5NS^2 + 2KO + 4HO = NH^3 + C^4H^6S^2 + 2(KO,CO^2)$] — Sulphocyanide of ethyl heated with an alcoholic solution of protosulphide of potassium, immediately forms protosulphide of ethyl and sulphocyanide of potassium:

$$C^4H^5C^2NS^2 + KS = C^4H^5S + C^2NKS^2.$$

The alcoholic solution of sulphocyanide of ethyl does not precipitate the salts of the heavy metals.

¶ Oxysulphocyanide of Ethyl. $C^6H^5NSO^2 = C^4H^5O,C^2NSO$.

DEBUS. *Ann. Pharm.* 82, 253; abstr. *Pharm. Centr.* 1853, 81; *N. Ann. Chim. Phys.* 36, 237; *N. J. Pharm.* 22, 311; *Jahresber*, 1852, 565, 568.

Oxysulfocyansaures Aethyloxyd. — Discovered by Debus in 1852.

Formation and Preparation. 1. By the action of nitrous acid on xanthamide (p. 441), protoxide of nitrogen being formed at the same time and sulphur precipitated:

$$C^6H^7NS^2O^2 + NO^3 = C^6H^5NSO^2 + S + NO + 2HO.$$

Xanthamide suspended in water and exposed to the action of a stream of nitrous acid gas, melts and forms at first a colourless liquid, which however soon turns yellow and deposits a quantity of small crystals: a colourless gas (nitrous oxide) is at the same time evolved. When the decomposition is complete, if the product be washed with water and then digested in alcohol, the crystals dissolve, and a yellow oil is left behind. This oil remained fluid for several months and then solidified in the form of pure sulphur.

— From the alcoholic solution, the compound $C^6H^5NSO^2$ separates in crystals resembling urea. — 2. By the action of protochloride of copper on xanthamide. When a neutral solution of protochloride of copper is added to an alcoholic solution of xanthamide, the liquid first assumes a blood-red colour, but afterwards becomes colourless and exhibits an acid reaction. Sulphur is also precipitated, and the liquid filtered from this precipitate at the termination of the action, first yields crystals of a compound of xanthamide and cuprous chloride ($C^6H^7NS^2O^2,Cu^2Cl$), and afterwards long, white prismatic needles of oxysulphocyanide of ethyl; the mother-liquor contains hydrochloric acid and excess of cupric chloride:

$$3C^6H^7NS^2O^2 + 4CuCl = 2(C^6H^7NS^2O^2,Cu^2Cl) + C^6H^5NSO^2 + 2HCl + S.$$

Properties. Crystallizes from strong alcoholic solutions, in thin, white prisms; from dilute solutions, in needles grouped in dendritic masses. The aqueous and alcoholic solutions, when evaporated at ordinary temperatures, yield the whole of the compound in its unaltered state; when these solutions are boiled, the greater part of the compound volatilizes undecomposed, together with the watery or alcoholic vapours; if the operation be performed in a retort, the neck becomes completely covered with long prismatic needles. — The compound melts below 100°, and on cooling solidifies in a radiated crystalline mass like nitre. At higher temperatures, it partly volatilizes undecomposed, and is partly resolved into new compounds, among which the sulphur-compounds of ethyl may be recognized by their characteristic odour. — The solutions of this compound are neutral.

			Debus.
6 C	36	41·37	40·53 .... 41·13
5 H	5	5·74	5·66 .... 6·17
N	14	16·09	16·17
S	16	18·40	20·08
2 O	16	18·40	
C^4H^5O,C^2NSO	87	100·00	

Decompositions. Nitric acid of sp. gr. 1·4 decomposes oxysulphocyanide of ethyl, with evolution of nitrous acid; oil of vitriol blackens it, and evolves sulphurous acid; hydrochloric acid dissolves it readily, forming decomposition-products not yet examined. — When boiled with baryta-water, it is decomposed, with formation of alcohol, ammonia, and carbonate of baryta, and precipitation of sulphur.

$$C^6H^5NSO^2 + 2BaO + 4HO = C^4H^6O^2 + NH^3 + 2(BaO,CO^2) + S.$$

The solutions of this compound are not precipitated by nitrate of silver, corrosive sublimate, or bichloride of platinum.

Combinations. Oxysulphocyanide of ethyl dissolves in *water* and in *alcohol.* (Debus.) ¶.

Chlorocyanide of Ethyl ?

AIMÉ, *Ann. Chim. Phys.* 64, 221; abstr. *Ann. Pharm.* 23, 254; abstr. *J. pr. Chem.* 12, 62.

This compound is obtained by passing dry chlorine gas through alcohol containing cyanide of mercury; condensing the vapours evolved in consequence of the rise of temperature in a cooled U-tube; and washing the distillate with water to free it from alcohol.

Liquid of sp. gr. 1·12; boils below 50°; smells like chloride of cyanogen; excites a copious flow of tears, and tastes like hydrocyanic acid.

Its composition is expressed by the formula $C^6H^5NClO = C^4H^5O, C^2NCl$. [No analysis is given.]

Burns with a purple flame, emitting a vapour which precipitates a solution of silver. Aqueous ammonia decomposes it immediately, with evolution of gas. The compound decomposes slowly under cold water, quickly under hot water. The alcoholic solution decomposes in 24 hours, leaving a crystalline mass, easily soluble in water. — The compound dissolves in wood-spirit, ether, and alcohol, and is precipitated from its alcoholic solution by water. (Aimé.) Liebig (*Ann. Pharm.* 23, 257) justly regards this investigation as unsatisfactory.

Chlorocyanide of Formic Ether ? $C^8H^6NClO^4 = C^6H^6O^4, C^2NCl$.

STENHOUSE. *Ann. Pharm.* 33, 92; also *J. pr. Chem.* 26, 133; also *Phil. Mag. J.* 18, 29.

Preparation. 1. Four ounces of cyanide of mercury are agitated or heated in a tubulated retort, so that the alcohol may become saturated with the cyanide of mercury; and dry chlorine gas is passed through the tubulus to the bottom of the retort, which is agitated from time to time to facilitate the solution of the cyanide, and kept constantly cool by immersion in cold water, as otherwise the chloride of cyanogen would escape in the form of gas, instead of being absorbed by the alcohol. As soon as, in consequence of the continued passage of the chlorine, the temperature of the liquid rises, carbonic acid escapes with violent effervescence, and crystals of sal-ammoniac are deposited in large quantities, the stream of gas must be interrupted, and the liquid heated after being mixed with water. The sal-ammoniac then dissolves in the water, whilst this compound is deposited in needles, which continually increase in size; the mother-liquid is then to be decanted, the crystals thrown on a filter, washed with cold water till every trace of acid and chloride of mercury is removed, and then dried. If the passage of the chlorine be too long continued, heavy hydrochloric ether is formed, which adheres tenaciously to the crystals, imparting to them its odour and a greasy feel, and lowering their melting point.

2. Strong aqueous hydrocyanic acid prepared from ferrocyanide of potassium and sulphuric acid, is heated to the boiling point, its vapour

passed into alcohol, and chlorine gas passed into the alcohol as in (the containing vessel being carefully cooled, till the liquid efferves strongly, and deposits sal-ammoniac. The production of sal-ammoni arises from a decomposition of chloride of cyanogen by water:

$$C^2NCl + 4HO = 2CO^2 + NH^4Cl.$$

White silky needles, resembling sulphate of quinine; melting w partial sublimation at 120°; neutral to vegetable colours; tasteless, a inodorous. (Stenhouse.)

				Stenhouse.
8 C	48·0	35·45		35·89
6 H	6·0	4·42		5·02
N	14·0	10·34		10·39
Cl	35·4	26·15		26·01
4 O	32·0	23·64		22·69
$C^8H^6NClO^4$	135·4	100·00		100·00

(Stenhouse supposes the body to contain 1 At. H more, making its formula $C^8H^7NClO^4$; according to this formula, Liebig regards it as a compound of 3 aldehyde with 2 At. chloride of cyanogen and 2 At. water:

$$3C^4H^4O^2 + 2C^2NCl + 2HO = 2(C^8H^7NClO^4);$$

according to Berzelius (*Jahresber.* 23, 523), it may be regarded as a compound c chloric of ethyl and a cyanide of elayl:

$$C^4H^5ClO^4 + C^4H^3N = C^8H^7NClO^4.$$

The vapour of the compound burns, when set on fire, with a lar yellow flame, which does not deposit soot. With boiling solution potash, the compound gives off ammonia, and forms a dark bro liquid.

It dissolves sparingly in cold water or aqueous ammonia, and from solution in either of these liquids at a boiling heat, it separates in original state on cooling. From its solution in gently heated oil of vit it does not separate on cooling, but, on addition of water, it separates its original state. Does not dissolve in hydrochloric acid, but is reac soluble in ether and alcohol, and precipitated from these solutions water. (Stenhouse.)

Acetate of Ethyl. $C^3H^8O^4 = C^4H^5O, C^4H^3O^3$.

LAURAGAIS. *Journ. des Sçavans.* 1759, 324.
WESTENDORF. Dissert. de optima acetum conc. ejusdemque naphtl conficiendi ratione. Gött. 1772.
BUCHOLZ. *Taschenb.* 1803, 57; 1807, 33.
VOIGT. *Taschenb.* 1781, 5; 1782, 4; 1783, 1; 1784, 184.
SCHEELE. *Opusc.* 2, 138; also *Crell. Ann.* 1784, 2, 342.
BERTR. PELLETIER. *Crell. Ann.* 1786, 2, 323.
HERMBSTADT. *Phys. chem. Vers.* 1, 152.
J. PELLETIER. *Scher. J.* 6, 438.
CHENEVIX. *Gilb.* 32, 192.
SCHULZE, GEHLEN, and F. D. LICHTENBERG. *A. Gehl.* 5, 672.
N. E. HENRY. *Ann. Chim.* 58, 199; also *N. Gehl.* 1, 720. — *J. Pha* 13, 127.

THÉNARD. *Mém. de la Soc. d'Arcueil*, 1, 153; 2, 16; abstr. *N. Gehl.* 4, 42.
P. F. G. BOULLAY. *N. Gehl.* 4, 42; also *Gilb.* 44, 285.
DUFLOS. *N. Tr.* 6, 1, 307; 6, 2, 136.
J. DUMAS & POL. BOULLAY. *J. Pharm.* 14, 113; also *Schw.* 52, 337, and 432.
LIEBIG. *Ann. Pharm.* 5, 34; also *Pogg.* 27, 615. — *Ann. Pharm.* 30, 144.

Acetic ether, Vinic or *Ethylic Acetate, Essignaphtha, Essigäther, Essigvinester, Essigsaures Aethyloxyd, Ether acétique, Acetate d'Oxyde d'Ethyle.* — Discovered by Lauragais in 1759.

Formation. 1. By heating alcohol with acetic acid. The more anhydrous the two liquids, the more quickly and abundantly do they produce the compound ether; but in all cases, to render the quantity of the ether in the distillate sufficient to be separated by water, it is necessary to repeat the distillation several times, continually pouring the distillate back again. — This is doubtless the reason of the statement made by Scheele, Körner, Dolfuss, Bucholz, Schulze, Gehlen, and Lichtenberg, that acetic acid distilled with alcohol yields no acetic ether, unless a small quantity of a strong mineral acid be added; while, on the other hand, Lauragais, Fourcroy, Pelletier, senr., & J. Bell, Spielmann, Westendorf, Hermbstädt, Leonhardi, Richter, Chenevix (*Gilb.* 72, 192), Thénard, Boullay, N. E. Henry, and others, probably because they cohobated the product more frequently, obtained the acetic ether merely by distilling acetic acid with alcohol. — A small quantity of acetic ether is formed by placing acetic acid for a considerable time in contact with absolute alcohol, even at ordinary temperatures. (Boullay, *Bull. Pharm.* 1, 111.) Even mixtures containing alcohol and acetic acid in the dilute state, such as wine-lees, or wine which has passed [partially] into the state of acetous formation, or vinegar [still containing a portion of alcohol not converted into acetic acid], yield by distillation a kind of brandy or vinegar containing a small quantity of acetic ether, which imparts to the brandy a peculiar taste and odour. (Voigt, *Taschenb.* 1783; Derosne, *Ann. Chim.* 68, 331; also *Gilb.* 32, 202; Mojon, *J. Phys.* 75, 55; Salzer, *Repert.* 12, 255.) A portion of this ether was perhaps formed before the distillation by the continued contact of the two bodies. — But the presence of sulphuric, hydrochloric, nitric or hydrofluoric acid (Scheele), or of phosphorus, arsenic, or oxalic acid (but not phosphoric, sulphurous, or tartaric acid (Thénard), greatly accelerates, by its water-forming power, the production of the acetic ether, so that in many cases a single distillation is sufficient to convert the greater part of the alcohol into acetic ether. — A mixture of 4 pts. absolute alcohol, 4 pts. glacial acetic acid, and 1 pt. oil of vitriol, set aside for a few days, forms a small quantity of acetic ether, which separates on addition of water. (Catel, *A. Gehl.* 5, 692.) — Chloride of arsenic acts like the mineral acids in accelerating the formation of the ether. (Duflos, *N. Tr.* 6, 2, 136.) — Aqueous solution of chloride of zinc, of such strength as to boil at 140°, forms with alcohol alone, merely a trace of vinic ether, but with alcohol and acetic acid, it facilitates the formation of acetic ether, just as sulphuric acid does. (Mitscherlich, *N. Ann. Chim. Phys.* 7, 10.) — Acetic ether is likewise obtained by distilling alcohol with oil of vitriol and an acetate. If the quantity of sulphuric acid is at most sufficient to saturate the base of the acetate, the

formation of acetic ether goes on as slowly as when acetic acid and alcohol are distilled together without addition of another acid; but if, as Scheele recommends, the sulphuric acid be added in excess, a single distillation is sufficient to convert nearly all the alcohol into acetic ether. — If a stream of carbonic acid gas be passed through a solution of acetate of potash in absolute alcohol, so as to throw down carbonate of potash (I, 127), the supernatant liquid is found to contain a considerable quantity of acetic ether. (Pelouze.) — On the formation of acetic ether under the influence of the stronger acids, see also Jonas (*Arch. Pharm.* [2], 72, 9; *Pharm. Centr.* 1850, 479.)

2. One pt. of vinic ether gradually mixed with 2 pts. of oil of vitriol, and then with 1 pt. of glacial acetic acid, acquires the odour of acetic ether, and yields that product by distillation. (Duflos, *N. Tr.* 6, 1, 307.)

3. When 3 pts. of sulphovinate of lime are distilled with 1 pt. of glacial acetic acid, or when sulphovinate of potash is distilled with acetate of potash, or a strong solution of phosphovinic acid with acetate of potash, a large quantity of acetic ether is obtained (Liebig, *Ann. Pharm.* 13, 31 and 32, and *Chim. organ.* 1, 399 and 400):

$$C^4H^5CaO^2,2SO^3 + C^4H^4O^4 = C^8H^8O^4 + CaO,SO^3 + HO,SO^3.$$

and:

$$C^4H^5KO^2,2SO^3 + C^4H^3KO^4 = C^8H^8O^4 + 2(KO,SO^3).$$

Acetic ether also passes over in the distillation of sulphovinic acid with acetic acid. (Mitscherlich.) This however does not prove that in the preparation of acetic ether from alcohol, oil of vitriol, and acetic acid, the formation of acetic ether is preceded by that of sulphovinic acid; for this mixture contains no sulphovinic acid—not even when part of the acetic ether is distilled off from it. Moreover the formation of the acetic ether is powerfully assisted by other mineral acids—hydrochloric acid, for example; and in this case we cannot suppose that it is preceded by the formation of hydrochloric ether; for hydrochloric acid is much less disposed to form hydrochloric ether with alcohol than to produce acetic ether with alcohol and acetic acid; and hydrochloric ether cannot be converted into acetic ether by distillation with acetic acid. (Mitscherlich, *N. Ann. Chim. Phys.* 7, 10.)

4. In the decomposition of chloride of ethylene by water under the influence of the sun's rays. (Mitscherlich, p. 380.)

Preparation. Equal parts of alcohol and glacial acetic acid are distilled together, the distillate being frequently poured back, and the distillation continued from 3 to 15 times, almost to dryness, but lastly till only half the liquid has distilled over; the acetic ether may then be separated from the distillate by caustic potash or lime-water. — Lauragais and Pelletier made use of glacial acetic acid prepared from acetate of copper (*Kupferspiritus*, p. 288); the quantity of acetic ether obtained amounted to 0·8 of the alcohol used. Spielmann, Westendorf, and Thénard, used the acetic acid separated by oil of vitriol from an anhydrous acetate; Thénard obtained 98 pts. of acetic ether from 100 pts. of alcohol.

2. A mixture of alcohol and glacial acetic acid in equal parts is distilled with addition of a small quantity of oil of vitriol. (Scheele, Thénard.) — 100 pts. alcohol, 63 glacial acetic acid, and 17 oil of vitriol, yield 125 pts. of a distillate consisting almost wholly of acetic ether, which may be purified by placing it for half an hour in contact with 10 pts. of hydrate of potash. — 100 pts. alcohol, 100 pts. acetic acid, and

50 pts. oil of vitriol, yield 125 pts. of acetic ether. (Schulze.) — 100 pts. of alcohol of 36° Bm. and 17 pts. strong acetic acid of 10° or 11° Bm. distilled with 17 pts. oil of vitriol, the distillate being frequently returned, yield 122 pts. of pure acetic ether. (Guibourt, *J. Pharm.* 3, 417.)

3. An acetate is distilled with a mixture of alcohol and a quantity of oil of vitriol somewhat more than sufficient to saturate the base. — The alcohol may first be poured upon the acetate, and then the oil of vitriol, or the alcohol and oil of vitriol may be first mixed and then poured upon the acetate. — Henry, from 100 pts. alcohol, 100 pts. acetate of copper, and 100 pts. oil of vitriol, obtained 107 pts. of acetic ether, which however appeared to contain a little vinic ether. — Voigt distils 10 pts. of alcohol with 16 pts. acetate of potash and 6 pts. oil of vitriol. — Westrumb, 2 pts. alcohol with 2 pts. acetate of potash and 1 pt. oil of vitriol. — Liebig distils 10 pts. of pounded crystallized acetate of soda with a mixture of 15 pts. oil of vitriol and 6 pts. 85 per cent. alcohol at a gentle heat at first, but afterwards at a tolerably strong heat; mixes the distillate in a tubulated retort with a sufficient quantity of potash to neutralize it; introduces into the distillate an equal volume of chloride of calcium; and rectifies after a few hours in the water-bath. In this manner, he obtains 6 pts. of acetic ether, which may be freed from any residual alcohol by again digesting it with chloride of calcium, then pouring it off and rectifying. Any vinic ether that may be mixed with it passes over at the commencement of the distillation. — Sébille-Auger (*J. Chim. méd.* 8, 237) mixes 30 kilograms of pulverized and dehydrated acetate of soda with 43 litres of alcohol of 32°, in a copper still provided with a silver condensing tube, and then adds 18 kilograms of oil of vitriol [which quantity however is but just sufficient to saturate the soda]. A large portion of the acetic ether is driven over by the heat evolved on adding the oil of vitriol; afterwards the distillation is carried almost to dryness by application of heat without, and in this manner there is obtained 56 kilogr. of crude acetic ether, which is shaken up and set aside with 1 kilogr. of slaked lime, then decanted and distilled, the first distillate which is yellow and turbid, and the last which is brown and acid, being kept apart. The product thus obtained is 40 kilogr. of pure acetic ether of sp. gr. 0·90, containing only small quantities of alcohol and water. — Fiedler mixes 16 pts. of crystallized acetate of lead with 4 pts. [too little] oil of vitriol and 6 pts. alcohol; Dingler (*A. Tr.* 12, 1, 131), 16 pts. crystallized acetate of lead with 10 pts. oil of vitriol and 16 pts. alcohol. — Bucholz mixes 40 pts. of crystallized acetate of lead with 23 pts. oil of vitriol and 20 pts. of 85 per cent. alcohol; distils off 24 pts. of pure acetic ether; then changes the receiver and collects 4 pts. of a liquid, from which, by agitation with caustic potash, 1½ pt. acetic ether separates and rises to the surface. He then agitates the whole of the acetic ether with caustic potash, separates it therefrom by a funnel, and rectifies it. — 19 pts. crystallized acetate of lead distilled with 9 pts. fuming sulphuric acid and 6 pts. alcohol of sp. gr. 0·835, yield 10·4 pts. of crude acetic ether, which, when shaken up with aqueous carbonate of potash and rectified, yields 7·75 pts. of acetic ether of sp. gr. 0·888. (Bette, *Ann. Pharm.* 31, 204.) — Liebig distils a mixture of 16 pts. anhydrous acetate of lead (dehydrated by melting it in a basin and stirring constantly), 5 pts. oil of vitriol, and 4½ pts. absolute alcohol, and obtains 6 pts. of acetic ether, which may be separated by agitation with water, and then freed from vinic ether by heating it to 40°. This acetic ether is then shaken up with aqueous carbonate of soda to remove sul-

phurous and free acetic acid, and then digested with lumps of chloride of calcium renewed from time to time; the chloride of calcium combines with all the water, and settles to the bottom in a layer, from which the acetic ether is poured off and rectified.

Acetic ether may be purified from alcohol by agitation with water, solution of potash, or chloride of calcium; from acetic and sulphurous acid by agitation with potash, carbonate of potash, or lime, which however must not be allowed to act long or at high temperatures, otherwise they will decompose it; from water by chloride of calcium; and from any vinic ether that may be present, by fractional distillation, the vinic ether being the more volatile of the two. — To obtain acetic ether perfectly free from alcohol, for analysis, Dumas & Boullay shook it up with water, fifteen times, using fresh water each time, and thereby raised the vapour-density from 2·40 to 3·06; by this treatment, however, the greater part of the acetic ether was taken up by the water.

[On the preparation of acetic ether, see also: H. Becker (*Arch. Pharm.* [2], 62, 163; 72, 15 and 147); Schenkel & Rieckher (*Jahrb. pr. Pharm.* 20, 193); Mohr (*Arch. Pharm.* [2], 65, 1); Marsson (*Arch. Pharm.* [2], 66, 257)].

Properties. Transparent, colourless, mobile liquid. Sp. gr. 0·812 (Hermbstädt); 0·862 (Chenevix); 0·866 at 7° (Thénard); 0·882 at 18° (Gehlen); 0·90691 at 0° (Pierre, *N. Ann. Chim. Phys.* 19, 207); 0·91046 (H. Kopp, *Pogg.* 72, 1); 0·906 at 17·5° (Marsson); 0·903 at 17° (H. Becker); 0·932 at 20°. (Gössmann, *Arch. Pharm.* [2] 73, 3.) — Boiling point 71°, at 0·75 met. pressure (Thénard); 74° at 0·76 met. (Dumas & Boullay); 70·14° at 0·7665 met. (Pierre); 74·3° at 0·76 met. (H. Kopp); 77·5° at 27″10‴ (in a silver vessel; pure acetic ether is easily heated above its true boiling point) (H. Becker); 83° in a glass vessel (Gössmann); 74·6° at 0·762 met. (Andrews, *Chem. Soc. Qu. J.* 1, 27); 74° (Person, *Compt. rend.* 23, 524). — Vapour-density = 3·06 (Boullay and Dumas). Has an agreeable odour and a pleasant astringent taste; does not redden litmus.

			Dumas & Boullay.	Liebig.
8 C	48	54·55	53·95	54·47
8 H	8	9·09	8·72	9·67
4 O	32	36·36	37·33	35·86
$C^8H^8O^4$	88	100·00	100·00	100·00

	Vol.	Density.
C-vapour	8	3·3280
H-gas	8	0·5544
O-gas	2	2·2186
Vapour of Acetic ether	2	6·1010
	1	3·0505

Decompositions. 1. Acetic ether burns when set on fire with a yellowish white flame, giving off vapours of acetic acid, and leaving that acid in the liquid state. (Scheele, Thénard.) In the lamp without flame it behaves like ether and alcohol. When it is burnt in Böttger's glow-lamp having an asbestus wick and a cap (p. 209), a transparent and colourless distillate is obtained which has a sp. gr. of 0·992, reddens litmus, and has an odour not so unpleasant as that of the lampic obtained from vinic ether, but more like that of acetic ether. It produces turbidity with nitrate of silver, and forms after a while a greyish white precipitate. But it does not reduce the solutions of mercury, gold, or

platinum, even at a boiling heat, neither does it become coloured when heated with oil of vitriol. (R. Böttger, *J. pr. Chem.* 12, 337; also *N. Br. Arch.* 13, 275.) Acetic ether kept in a bottle half full of air quickly turns sour. — 3. It absorbs chlorine gas, quickly at first and with great evolution of heat, afterwards more slowly, giving off a large quantity of hydrochloric acid gas mixed with chloride of ethyl, a small quantity of acetic acid being formed at the same time. In this reaction, the acetic ether is first converted for the most part into $C^8Cl^2H^6O^4$ (Malaguti), then by continued action of the chlorine, into $C^8Cl^3H^5O^4$, then into $C^8Cl^4H^4O^4$, then into $C^8Cl^5H^3O^4$, then into $C^8Cl^6H^2O^4$, then into $C^8Cl^7HO^4$, and finally into $C^8Cl^8O^4$. (Leblanc.)— 4. Acetic ether distilled with nitric acid yields acetic acid, and, according to Henry, leaves a residue containing a small quantity of oxalic acid. — 5. When distilled with oil of vitriol, it yields vinic ether and acetic acid. (Boullay.) Heated with an equal weight of hydrochloric acid, it yields chloride of ethyl in the distillate, and acetic and hydrochloric acid in the residue. (Duflos.) — 7. Distilled with chromic and sulphuric acid, it yields acetic acid and oxygen-ether (aldehyde.) (Duflos, *Berl. Jahrb.* 27, 1, 84.) — 8. In contact with water it quickly turns sour, that liquid taking up the acetic acid. (N. E. Henry.) — 9. Aqueous potash distilled with an aqueous solution of acetic ether, decomposes it quickly, with formation of acetate of potash (Scheele); in this case, according to Chenevix and Thénard, hydrated alcohol distils over; and, according to Thénard, 30 pts. of acetic ether yield 17 pts. of acetate of potash, and somewhat more than 15 pts. of alcohol (a portion of the alcohol was lost); the same decomposition is exhibited when vapour of acetic ether is passed through aqueous potash. (Boullay.) An acetate is also formed when acetic ether is kept in contact for four years at ordinary temperatures with potash, lime, magnesia, ferroso-ferric oxide or mercuric oxide; with mercuric oxide it forms mercurous as well as mercuric acetate. Zinc and iron also form small quantities of acetate; but ferric oxide, arsenious acid, antimony, bismuth, tin, and copper, have no action upon it. (N. E. Henry.) — 10. A mixture of lime and hydrate of potash absorbs acetic ether with great evolution of heat, and when strongly heated with it, gives off a large quantity of hydrogen gas, and forms acetate of potash (Dumas & Stas, *Ann. Chim. Phys.* 73, 152):

$$C^8H^8O^4 + 2(HO,KO) = 2C^4H^3KO^4 + 4H.$$

Acetic ether dehydrated over chloride of calcium is not decomposed by hydrate of potash which has been freed by fusion from excess of water. (Duflos.)

11. Potassium decomposes acetic ether, evolving great heat, often sufficient to set the liquid on fire, and converts it into a mass which appears to contain acetylite or even aldehydate of potash, besides ethylate of potassium. (Löwig & Weidmann. *Pogg.* 50, 98.) When potassium is added by small portions to excess of acetic ether, the liquid being cooled from without during the addition of the potassium, but afterwards heated to the boiling point: it deposits on cooling, white saline flocks, or if a tolerably large quantity of potassium has been used, solidifies in a crystalline mass. This mass dissolves in water, while the undecomposed portion of the acetic ether separates out. The aqueous solution when distilled, gives off a mixture of acetic ether and alcohol, and leaves a brown alkaline liquid, which when placed over mercury, greedily absorbs oxygen, and thereby loses the power of precipitating the metal from

nitrate of silver at a gentle heat. The brown liquid mixed with sulphuric acid deposits flakes of brown resin, and if subsequently distilled out of contact of air, yields an acid like acetic acid and not possessing the odour of aldehyde; this acid dissolves oxide of silver, but deposits the metal on the application of heat, and forms acetate of silver when heated with excess of oxide of silver. (Löwig & Weidmann.)—[Löwig & Weidmann give for hypothetically anhydrous hypoacetylous acid, the formula $C^4H^3O^{14}$, and express the reaction by the equation:

$$2C^8H^8O^4 + 3K = KO,C^8H^{10}O^2 + 2(KO,C^4H^3O^{14});$$

But ethylate of potassium is not $KO,C^8H^{10}O^2$, but $KO,C^4H^5O = C^4H^5KO^2$. The following equation is simpler:

$$C^8H^8O^4 + 2K = C^4H^5KO^2 + C^4H^3KO^2.$$

The latter body would be aldehyde having 1 H replaced by 1 K, and when dissolved in water, would form potash and aldehyde, which however, if the air were not completely excluded, would be partially converted into acetic acid. Löwig & Weidmann, however, did not obtain any indication of the presence of aldehyde.]

Combinations. Acetic ether dissolves in 7 pts. of *Water* (Thénard), in 9 pts. (Gehlen), forming a solution which when recently prepared does not redden litmus.—¶ According to Mohr (*Arch. Pharm.* [2], 65, 1) it dissolves in 11 or 12 times its weight of water at ordinary temperatures; according to Becker (*Arch. Pharm* [2], 72, 15 and 147) it dissolves at ordinary temperatures in about 12 pts. of water, and dissolves from $\frac{1}{30}$ to $\frac{1}{33}$ of that liquid; according to Marsson (*Arch. Pharm.* [2], 66, 257) it gives up scarcely 5 per cent. of its volume to an equal volume of water at 17·5°. ¶

Acetic ether dissolves *Phosphorus*, forming a solution precipitable by water. (N. E. Henry.)

Dissolves only 0·6 per cent. of *Sulphur*. (Favre).

Mixes with strong *mineral acids*. (Westendorff.)

If previously dehydrated by chloride of calcium, which, together with the water, settles to the bottom forming an oily stratum, it dissolves large additional quantities of *chloride of calcium*, forming a thick mixture which solidifies in a stiff crystalline magma. This crystalline compound, which resembles the alcoholates and may be obtained quite dry by pressure between paper, gives off the ether at the heat of the water-bath, without fusion and in a state of the greatest purity, and is resolved by contact with a small quantity of water or by exposure to moist air, into aqueous chloride of calcium and free acetic ether. (Liebig.)

Acetic ether is capable of combining with *Bichloride of Tin*. (Lewy.)

It mixes in all proportions with *Alcohol* and *Ether*, and is separated from the latter by water. *Sweetened Acetic Acid, versüsste Essigsäure, Spiritus dulcificatus, Liquor anodynus vegetabilis Westendorfii*, is a mixture of acetic ether and alcohol.

It mixes with concentrated *Acetic acid*. (Westendorf.)

It dissolves oils both fixed and volatile, also resins, many organic acids, &c.

END OF VOLUME VIII.

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REPORT

OF

THE SIXTH ANNIVERSARY MEETING

OF THE

CAVENDISH SOCIETY.

THE Anniversary Meeting of the Cavendish Society for the year 1853 was held at the rooms of the Chemical Society, No. 5, Cavendish Square, on Monday, the 1st of March, at three o'clock in the afternoon.

The Chair was taken by THOMAS GRAHAM, ESQ., F.R.S., PRESIDENT, who called upon the Secretary to read

THE REPORT OF THE COUNCIL.

"THE statement which the Council have to submit to the Members at this the sixth Anniversary Meeting of the Cavendish Society, will not, they trust, be thought less satisfactory than that of any former year. The continued accession of new Members, who on joining the Society, become subscribers from the commencement, affords strong evidence of the high estimation in which all the works of the Society are held, and justifies the course pursued by previous Councils, in providing for the demand which now annually occurs for the books relating to past years. This constantly occurring addition of Members has raised the number of those who have subscribed for the years 1848, 1849 and 1850, the three first years of the Society, to about a thousand; yet as some of these have fallen off, from death and other causes, the income of the Society must be estimated at rather less than the sum derivable from a subscription list of that extent. The increase in the amount of subscriptions received since the last Anniversary Meeting, as compared with the statement of preceding years, is the more satisfactory, when considered in connexion with the unavoidable delay which has occurred in completing the works for 1852. This delay has been a source of much anxiety to the Council, and they trust the arrangements they have made for the future, will obviate a repetition of it.

"The Council, having entered into an agreement with PROFESSOR BISCHOF, of Bonn, by which the latter undertook to furnish to the Society, a new edition of his 'Elements of Chemical and Physical Geology,' written expressly for them, it was expected that the first volume of this work would have been ready for delivery, as one of those issued for 1852; it was found impossible, however, to get the work ready at so early a date, and therefore, another book has been substituted for it.

"Three works have been prepared for 1852, namely, the first volume of the 'Organic part of GMELIN's Hand-book of Chemistry,' the second volume of LEHMANN's 'Physiological Chemistry,' and an 'Atlas of Plates,' representing the Microscopic appearance of Crystalline and other substances relating to Physiological Chemistry, by DR. OTTO FUNKE. These works all possess considerable interest and importance, and will, it is confidently anticipated, add to the high character which the works of the Society have acquired in the estimation of scientific men.

"GMELIN, in the volume now issued, introduces the subject of Organic Chemistry, that department of the science which has been most prolific of late years, of new facts and theories. A considerable portion of the book is devoted to the generalities of Organic Chemistry, relating to the formation and properties of organic compounds—their transformations and decompositions,—their classification, and the theories which have been adopted with reference to their constitution. The subject has been well brought up to the present time, by the very judicious additions which have been made by MR. WATTS, the translator.

"The recent appearance of a new part of the German edition of GMELIN's work seems to justifiy the anticipation that it may be completed by the author at a sufficiently early period to admit of the uninterrupted progress of the translation.

"The second volume of LEHMANN's 'Physiological Chemistry,' which has been prepared as the second of the Society's books for 1852, treats of the animal fluids or juices, and completes this part of the subject.

"The third work which the Council have been enabled to furnish to the Members in return for the subscription of 1852, consists of a series of beautifully executed plates, containing highly characteristic microscopic representations of crystalline and organic objects, which are referred to by PROFESSOR LEHMANN in his 'Physiological Chemistry.' These plates have been recently produced in Germany as a Supplement to LEHMANN's work, and the Council, having ascertained that their reproduction in this country, with an equally perfect execution, would have involved a very considerable outlay, made an arrangement with the German publishers, by which they have been supplied with the number required for the Members of the Cavendish Society from the original engravings. The description of the plates has been translated for the Society by DR. PAUL.

"The works for the present year, 1853, are in progress of preparation. Part of the manuscript of the first volume of PROFESSOR BISCHOF's work has already been received, and the whole is prepared and only waiting the author's final revision. It will be printed with as little delay as possible. The translation of the third and last volume of LEHMANN's 'Physiological Chemistry' is being proceeded with, as also is the second volume of the Organic part of GMELIN's 'Hand-book.'"

Treasurer's Statement of the Receipts and Expenditure of the Cavendish Society, from the 1st of March, 1852, to the 26th of February, 1853.

Receipts.

			£	s.	d.
Balance from previous year			340	12	3
60	Subscriptions for	1848	34	8	0
66	Ditto	1849	66	18	0
72	Ditto	1850	73	2	0
137	Ditto	1851	140	11	0
606	Ditto	1852	633	12	0
95	Ditto	1853	99	15	0
			£1388	18	3

Expenditure.

	£	s.	d.
Stationery, Postage, Delivery of Books	14	12	0
Advertisements	7	18	0
Insurance	2	5	0
Collector's Commission	10	1	0
Secretary	90	0	0
Editorial expenses	151	10	0
Paper	153	1	0
Printing	275	5	6
Engravings	5	2	0
Binding and wrapping	84	19	8
	794	14	2
Balance in hand	594	4	1
	£1388	18	3

We have examined the above statement, and find it correct.

February 26th, 1853.

T. H. HENRY.
JOHN PERCY.

It was moved by Mr. Baigent, seconded by Mr. Edmund Greaves, and resolved,

"That the Report just read be received and adopted."

The Meeting then proceeded to the election of Officers for the ensuing year, and the following Gentlemen were declared to have been duly elected:—

President.

Professor Graham, F.R.S.

Vice-Presidents.

Arthur Aikin, F.G.S.
Jacob Bell, F.L.S.
Professor Brande, F.R.S.
Earl of Burlington, F.R.S.
Sir James Clark, M.D., F.R.S.
Walter Crum, F.R.S.
John Davy, M.D., F.R.S.
Michael Faraday, D.C.L., F.R.S.
J. P. Gassiot, F.R.S.
Sir. R. Kane, M.D., F R.S.
W. A. Miller, M.D., F.R.S.
Professor Wheatstone, F.R.S.

Council.

P. J. Chabot, M.A., F.R.A.S.
Warren De la Rue, Ph.D., F.R.S.
W. Ferguson, F.C.S.
J. J. Griffin, F.C.S.
T. H. Henry, F.R.S.
H. Bence Jones, M.D., F.R.S.
G. D. Longstaff, M.D., F.C.S.
T. N. R. Morson, F.L.S.
John Percy, M.D., F.R.S.
R. Porrett, F.R.S.
R. H. Semple, M.D.
W. Sharpey, M.D., F.R.S.
Alfred Smee, F.R.S.
E. F. Teschmacher, F.C.S.
Charles Tomlinson, Esq.
A. W. Williamson, Ph.D., F.C.S.

Treasurer.

Henry Beaumont Leeson, M.D., F.R.S., St. Thomas's Hospital.

Secretary.

Theophilus Redwood, Esq., 19, Montague Street, Russell Square.

It was resolved,

"That Mr. G. B. Buckton, Mr. Dugald Campbell, and Mr. James Tennant, be appointed Auditors for the ensuing year."

The following Resolutions were unanimously adopted:—

"That the thanks of the Meeting be given to the President, Treasurer, and Council, for their services to the Society."

"That the thanks of the Meeting be given to the Honorary Local Secretaries for their services to the Society."

"That the thanks of the Meeting be given to the Chemical Society for the use of their rooms on the present occasion."

The Meeting was then adjourned.

THEOPHILUS REDWOOD, Secretary,
19, Montague Street, Russell Square.

March 1st, 1853.

WORKS OF THE CAVENDISH SOCIETY.

1848.

1.—CHEMICAL REPORTS AND MEMOIRS. Edited by THOMAS GRAHAM, F.R.S. (Out of Print.)

2.—HAND-BOOK OF CHEMISTRY. By LEOPOLD GMELIN. Translated by HENRY WATTS, B.A., F.C.S. Vol. I.

1849.

3.—HAND-BOOK OF CHEMISTRY. By LEOPOLD GMELIN. Vol. II.

4.—HAND-BOOK OF CHEMISTRY. By LEOPOLD GMELIN. Vol. III.

5.—THE LIFE AND WORKS OF CAVENDISH. By Dr. GEORGE WILSON.

1850.

6.—HAND-BOOK OF CHEMISTRY. By LEOPOLD GMELIN. Vol. IV.

7.—HAND-BOOK OF CHEMISTRY. By LEOPOLD GMELIN. Vol. V.

1851.

8.—PHYSIOLOGICAL CHEMISTRY. By PROFESSOR LEHMANN. Translated by GEORGE E. DAY, M.D., F.R.S. Vol. I.

9.—HAND-BOOK OF CHEMISTRY. By LEOPOLD GMELIN. Vol. VI.

1852.

10.—HAND-BOOK OF CHEMISTRY. By LEOPOLD GMELIN. Vol. VII. (Organic Chemistry, Vol. I.)

11.—PHYSIOLOGICAL CHEMISTRY. By PROFESSOR LEHMANN. Vol. II.

12.—ATLAS OF PLATES RELATING TO PHYSIOLOGICAL CHEMISTRY. By DR. OTTO FUNKE.

(Supplement to LEHMANN'S PHYSIOLOGICAL CHEMISTRY.)

The first of the Society's publications, the volume of CHEMICAL REPORTS AND MEMOIRS, being out of print, those who now join the Society, and desire to obtain the whole of GMELIN'S CHEMISTRY, may be supplied with the first volume of this work on payment of half the Subscription for 1848; or the sixth volume of the HAND-BOOK OF CHEMISTRY may be substituted for the CHEMICAL REPORTS AND MEMOIRS as one of the books for 1848, so that the six volumes of GMELIN'S INORGANIC CHEMISTRY and THE LIFE OF CAVENDISH may be obtained for three years' subscription, namely, 1848, 1849, 1850. Members commencing from 1851 have the option of taking [illegible]E OF CAVENDISH instead of the sixth volume of GMELIN'S THEOPHR[illegible] the book which is given in addition to the first [illegible]'S PHYSIOLOGICAL CHEMISTRY for that year.

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Banbury—Thomas Beesley, Esq.
Bath—J. P. Tylee, Esq.
Beccles—W. E. Crowfoot, Esq.
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